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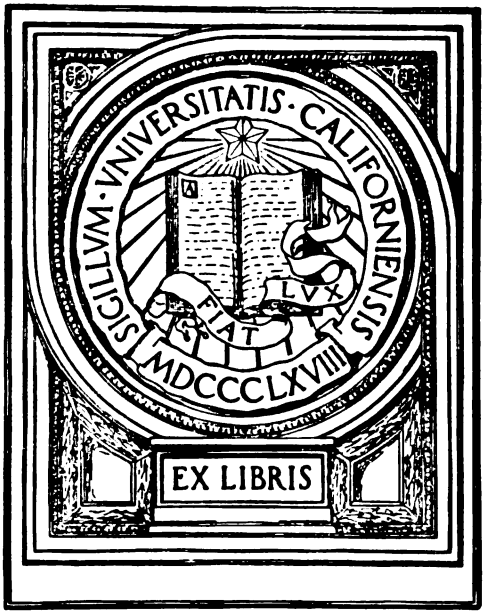

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A TEXT-BOOK OF PRACTICAL CHEMISTRY

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A TEXT-BOOK
OF
PRACTICAL CHEMISTRY

BY

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WITH 162 *ILLUSTRATIONS*

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PREFACE

THIS work is an attempt to place in the student's hands a Manual of Practical Chemistry which shall be a *reference book* in a convenient form.

Though not claiming in any way to be a specialist's book, it does aim at giving the student a thorough knowledge of general methods, so that he will be in a position to proceed to specialist work without difficulty.

The scope of the book does not allow of the inclusion of any very advanced work in Physical Chemistry; it indicates the basic lines along which the student may proceed and prepares him for seeking inspiration from the advanced theoretical text-books.

No great claim to originality is put forward, but a whole-hearted attempt has been made to indicate the *best methods* of doing everything. To this end a large number of original papers have been consulted, in addition to most of the text-books quoted in the literature of each branch, and the authors have also drawn on twelve years of teaching experience and their own experimental work.

It is believed that every source of special information has been acknowledged in the text.

The authors' thanks are due to Mr. J. S. Firth, B.Sc., for kindly reading through a large part of the MSS.; to Messrs. Clowes and Coleman for permission to make stereo-plates of the logarithm and atomic weight tables in their "Quantitative Analysis"; to Messrs. J. J. Griffin and A. Gallenkamp for permission to make sketches from diagrams of apparatus in their catalogues, and to the publishers for kindly help and advice throughout.

It is too much to hope that the first edition of a work of this kind will be free from errors, and the authors will be grateful for their attention being called to any which may have occurred.

G. F. H.
J. A. C.

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BOOK I.

INORGANIC PREPARATIONS.

CHAPTER I.

Introductory.—The following preparations are intended as a fairly complete course. They are not arranged in the order in which they are to be performed, but under suitable headings. Emphasis is laid on *general methods* of preparing the various classes of substances, and when these fail, or are inconvenient, the reason is given and the important exceptional cases dealt with in detail.

The following points should be carefully noted:

1. Scrupulous cleanliness should always be observed, in order that it may become a habit. Solutions should be filtered if there is any necessity whatever, and if put away overnight should always be covered up to exclude dust.

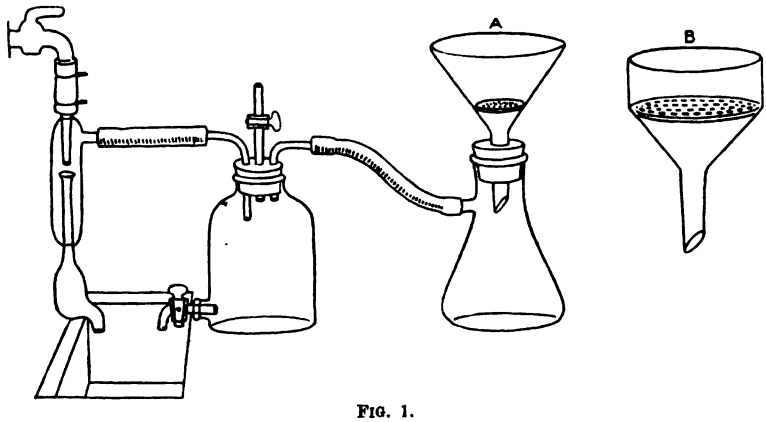

FIG. 1.

2. Great accuracy in weighing is seldom necessary, except when small quantities are being dealt with. A rough balance, turning to about 0·5 gm. may generally be used. Chemicals should never be put on the balance-pan, but on a clean piece of paper (which is counterpoised by a similar piece) or a clock-glass, or they may be weighed in the vessel in which the experiment is to be done. The yield of a preparation should be noted and compared with that demanded by theory or by the conditions of the experiment.

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3. The importance of keeping a note-book is too obvious to need more than the bare mention. The student should carefully avoid performing experiments in a mechanical way, without fully understanding the *reasons* for everything. *E.g.* if quantities of substances apparently demanded by an equation are not used, he should know exactly why.

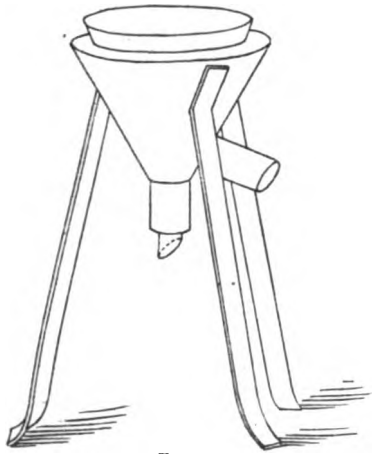

FIG. 2.

The following pieces of apparatus are described, as being in frequent use:

Filtration. — Crystalline preparations are filtered and drained by means of the filter-pump (Fig. 1). The large bottle *B* is to prevent water from *A* rushing into *C* if the water is inadvertently turned off before connection between *A* and *C* is broken. This should be done by opening *T* before turning off the water. *D* shows the funnel and porcelain filter-plate, the filter paper for which should be cut only *very slightly* larger than the plate.

On no account should fine precipitates be filtered with this apparatus, as the pores of the paper are rapidly stopped up by them and the process ceases. Nor should warm saturated solutions be filtered with it, or the substance will crystallise and stop up the funnel. Such solutions are filtered through an ordinary filter kept hot in a funnel-heater (Fig. 2). The stem of the funnel should be long enough just to clear the funnel-heater; if it is too long it will rapidly be stopped up by the substance crystallising in the cool projecting part.

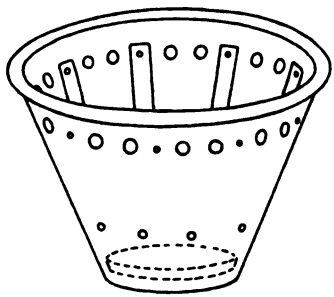

FIG. 3*a*.

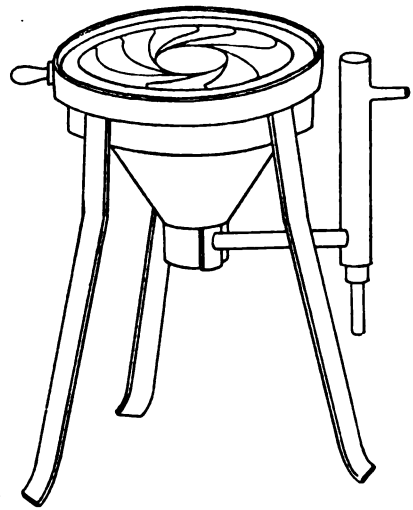

FIG. 3*b*.

Methods of heating.—Vessels other than crucibles should rarely be heated by a naked flame. A gauze, sand-bath, air-bath (Fig. 3*a*), water-bath (Fig. 3*b*),

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iron plate or asbestos card should be used, according to the nature of the preparation.

Crucibles may be heated in the "Midget" furnace (Fig. 4) or for higher temperatures in a muffle or crucible furnace (Fig. 5). The "Méker" furnace is useful, and small quantities of substances may be heated in one to very high temperatures with but a small gas consumption (Fig. 6).

Evaporation in vacuo is necessary when the substance in solution cannot stand high temperatures. This operation is carried out in a vacuum desiccator (Fig. 7), the water vapour being absorbed by strong sulphuric acid. The desiccator is evacuated by means of a good filter-pump or mechanical pump.

Methods of purification of substances.—Soluble substances are generally purified by recrystallisation, which is repeated as often as necessary. It is

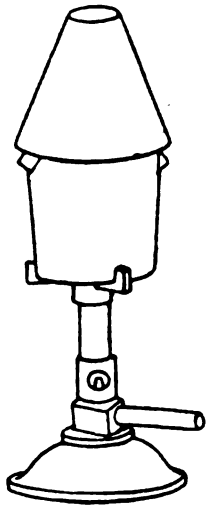

FIG. 4.

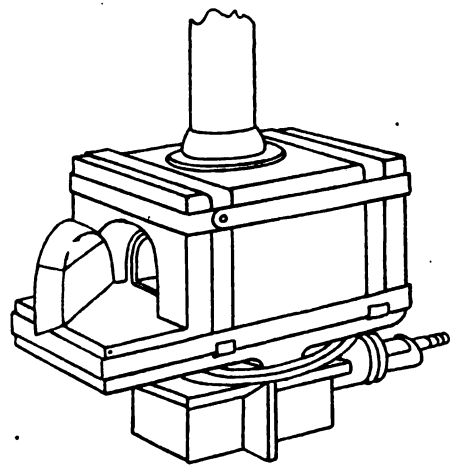

FIG. 5.

performed by adding the crude substance to boiling water till no more will dissolve, filtering if necessary (funnel kept hot), and cooling as rapidly as possible with shaking or vigorous stirring, in order to obtain crystals as small as possible. Such crystals are less liable to enclose portions of the mother liquor than large ones, which are obtained by allowing the hot saturated solution to cool slowly, or by allowing the cold saturated solution to evaporate at the room temperature. Large crystals, if specially required, should be obtained by dissolving and crystallising the *pure* substance.

If it is necessary to separate two substances which are both present in quantity but possess different solubilities, **fractional crystallisation** is used.

If there is much difference in the solubilities of the two substances, a preliminary partial separation may be made by extraction with a quantity of warm solvent insufficient to dissolve them both. If they are present in anything like equal proportions, the whole of the more soluble and a portion of the less soluble will dissolve. The residue thus consists of one substance only. The solution is then fractionated by collecting several fractions of

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crystals *either* (*a*) at different temperatures as the hot solution cools, *or* (*b*) at different times as spontaneous evaporation proceeds.

When it is seen (through a microscope, if necessary) that crystals of both substances are forming, the process is stopped, the liquor evaporated dry and the residue extracted as at first with sufficient solvent to dissolve all the more soluble, but not all the less soluble substance. Various portions of the less soluble substance are thus obtained which are put together and recrystallised from fresh solvent.

The less soluble substance does not necessarily separate out first; it may be present in sufficiently small amount to be completely dissolved before the more soluble substance.

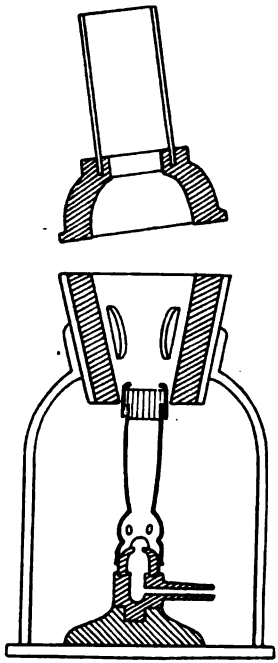

FIG. 6.

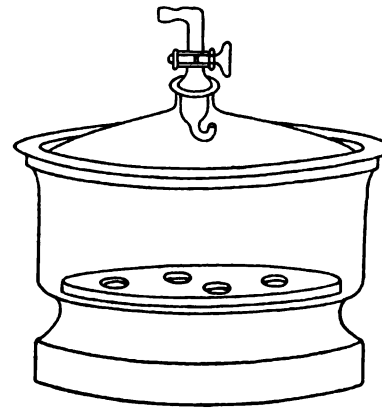

FIG. 7.

A quantitative separation of the substances is obviously impossible.

Distillation and Vacuum distillation. See Book IV. pp. 282-5.

Supersaturated solutions.—It frequently happens that a hot saturated solution will not crystallise at once on being cooled. It is said to be supersaturated, and crystallisation can be induced by (*a*) shaking, (*b*) scratching the sides of the vessel with a glass rod (when crystals will first form along the scratches), and (*c*) by "seeding" the solution with a fragment of the substance in solution. In some obstinate cases it may be necessary to leave the supersaturated solution in contact with a little of the solid for a considerable time.

(See Miers and Isaac, *J.C.S.*, 1906, 89. 413; *J.C.S.* abs. 1907, ii. 670; and Hartley and Thomas, *ibid.* 1013.)

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CHAPTER II.

PREPARATION OF GASES.

WHEN a gas is prepared by the action of a solid and a liquid in the cold, a Kipp generator is the most convenient apparatus (Fig. 8). The bulb *B* contains the solid. The tap *T* is opened and the liquid poured in *A* until *C* is full and the liquid rises well into *B*. *T* is then closed. The gas generated in *B* forces the liquid out of *B* back into *C* and up the tube into *A*, when the action ceases. *B* and about half of *C* are generally full of the gas, which is thus obtained at once on opening *T*. *D* is for cleaning purposes, and *F* is a funnel containing a reagent for preventing the escape of a noxious gas.

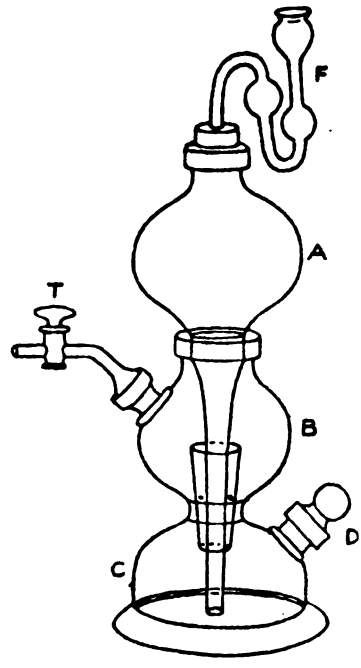

FIG. 8.

The following gases may be prepared in a Kipp.

Hydrogen.—Use granulated zinc and dilute sulphuric acid (1 : 8). If fairly pure H is necessary, pure zinc (arsenic-free) must be used. The action with sulphuric acid is very slow unless the zinc be coated with copper by treating it with copper sulphate solution before putting it into the apparatus. Absolutely pure hydrogen is obtained only by electrolysing barium hydrate solution.

Hydrogen sulphide.—Use ferrous sulphide and hydrochloric acid (1 volume of commercial acid : 1 volume of water).

Carbon dioxide.—Use marble and hydrochloric acid (1 : 1½).

Nitric oxide.—Use copper turnings and nitric acid (1 : 1½).

Chlorine.—Use bleaching powder (made into lumps) and strong hydrochloric acid (1 volume commercial acid : ½ volume of water).

N.B.—These gases may be dried by strong sulphuric acid if necessary, with the exception of hydrogen sulphide, which reacts with it readily thus :

$$H_2S + H_2SO_4 = SO_2 + S + 2H_2O.$$

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This gas is therefore dried by calcium chloride if necessary.

In any case, all the above gases before use should be passed through a wash-bottle containing a little water. This is to free them from acid fumes, spray, etc., from the Kipp.

The preparation of other gases frequently required is described below.

Oxygen.—Heat carefully a mixture of potassium chlorate 4 parts, manganese dioxide 1 part. As thus prepared it is slightly contaminated with chlorine. If required quite pure, it must be made by heating potassium chlorate alone. A higher temperature is necessary, and either a Jena flask or an iron retort (made for the purpose) should be used.

Hydrochloric acid gas is conveniently prepared by putting strong hydrochloric acid in a flask fitted with a delivery tube and dropping funnel, and dropping strong sulphuric acid slowly in from the funnel. The stream of gas can be regulated to a nicety.

The gas may also be obtained by mixing 2 parts of strong sulphuric acid, 1 part of water and 2 parts of common salt (all by *weight*). This mixture gives the gas only when warmed, and there is complete control over the rate of the reaction.

Chlorine.—If only a small quantity is required, the most convenient way is to drop strong hydrochloric acid from a dropping funnel on to solid potassium permanganate contained in a flask. Towards the end of the reaction the flask may be gently warmed.

Large quantities of chlorine are most economically prepared by heating manganese dioxide (lumps, not powder) with strong hydrochloric acid in a two-litre flask. Granular pyrolusite should be used, and fresh acid is introduced in the gaseous form by a delivery tube dipping beneath the liquid, thus avoiding undue dilution.

The large flask is heated on a water- or sand-bath, and the chlorine is washed with water to free it from hydrochloric acid, and dried (if necessary) by strong sulphuric acid.

Sulphur dioxide is sold in the liquid form in glass "syphons." If one of these is not available, the gas may be prepared by heating copper turnings with strong sulphuric acid.

Ammonia is most conveniently obtained by cautiously warming ·880 ammonia solution in a flask, and drying the evolved gas by quick-lime.

Nitrogen is obtained by passing air first through ·880 ammonia and then over red-hot copper turnings. The oxygen of the air is absorbed by the copper and the resulting copper oxide is at once reduced back to copper by the ammonia. The frequent renewals of the contents of the copper tube are thus entirely avoided.

$$2Cu + O_2 = 2CuO,$$

$$2NH_3 + 3CuO = N_2 + 3H_2O.$$

The gas should be washed with sulphuric acid (1 : 4) to free from excess of ammonia, and dried by strong sulphuric acid. The use of dilute acid to free it from ammonia is to avoid the danger of a great rise in temperature should a large excess of ammonia come over.

Small quantities of nitrogen may be prepared by carefully heating a

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solution of ammonium nitrite (sodium nitrite and ammonium chloride in molecular proportions).

$$NH_4NO_2 = 2H_2O + N_2.$$

The method is not recommended as it is difficult to control, and the nitrogen is generally contaminated with oxides of nitrogen, especially when the action becomes violent.

Nitrous oxide is obtained by heating ammonium nitrate in a flask fixed horizontally. A second flask may be used to condense some of the water formed by the reaction.

$$NH_4NO_3 = 2H_2O + N_2O.$$

Heat carefully, as the decomposition may become dangerously violent, especially when only a small quantity of ammonium nitrate is left.

Nitric oxide as obtained from copper and nitric acid is never pure. It generally contains a small proportion of nitrous oxide, which increases as the nitric acid becomes dilute. If required quite pure it may be prepared

(*a*) By dropping strong sulphuric acid very slowly on to an intimate mixture of sodium nitrite and ferrous sulphate.

(*b*) By slowly dropping a solution of sodium nitrite (20%) into a solution of ferrous chloride and hydrochloric acid. The residual solution from the H_2S Kipp, boiled in a large flask till free from H_2S, is excellent for this purpose.

Carbon monoxide is obtained by warming strong sulphuric acid and slowly dropping in formic acid, or a strong solution of sodium formate, from a dropping funnel.

$$H{\cdot}COOH - H_2O = CO.$$

It is cheaper to use oxalic acid,

$$H_2C_2O_4 - H_2O = CO + CO_2,$$

but the CO_2 produced at the same time has to be removed by passing the gas through several wash-bottles containing strong caustic soda solution, and finally through a tower filled with soda lime. The removal of the carbon dioxide from the somewhat rapid stream of gas is incomplete with one or two wash-bottles.

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CHAPTER III.

METALLIC OXIDES.

A. **Basic oxides.**—The following general methods are used for preparing metallic oxides (basic).

(i) The metal is heated in air or oxygen. This method is not much used, as in most cases combustion is very incomplete. Black-copper oxide, CuO, and litharge, PbO, are made in this way on the large scale, litharge being a by-product in the cupellation of lead-silver alloys in the extraction of silver from lead by Pattinson's method of eighths. CuO made thus nearly always contains much unoxidised copper, or, at any rate, cuprous oxide.

(ii) The carbonate of the metal is heated strongly, *e.g.*

$$CaCO_3 = CaO + CO_2.$$

This is a very useful method, as various carbonates occur naturally of sufficient purity to give a fairly pure oxide, *e.g.* $CaCO_3$, $MgCO_3$, $BaCO_3$, $SrCO_3$.

Otherwise the metallic carbonate is precipitated from a solution of some salt of the metal by adding the required amount of sodium carbonate. It is then filtered, washed, dried and ignited.

In a few cases, *e.g.* barium and strontium carbonates, an exceedingly high temperature is required to get rid of the carbon dioxide. In these cases, the required amount of carbon is mixed with the carbonate, and the reaction takes place much more readily, *e.g.*

$$BaCO_3 + C = BaO + 2CO.$$

(iii) By heating the nitrate of the metal, *e.g.*

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

This method rarely, if ever, gives a pure oxide, as the last traces of oxides of nitrogen are very difficult to remove; nevertheless it is a useful laboratory method.

(iv) The hydroxide of the metal is heated strongly. It is obtained by adding the required amount of sodium or ammonium hydroxide to a solution of a metallic salt, filtering, washing, drying and igniting. (Ammonium hydroxide is used only in the cases of the trivalent metals, iron(ic) chromium and aluminium; sodium hydroxide is used in other cases. The reason for this is that ammonium hydroxide either does not precipitate, or does so very incompletely, the hydroxides of the divalent metals. (See Qualitative Analysis under each metal.)

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(v) In a few cases none of the above methods are available. These are discussed in detail below.

Preparation of Metallic oxides by above Methods.

Method I.

1. **Preparation of copper oxide, CuO, from Copper.**—A known weight of precipitated copper (from the action of zinc on copper sulphate solution) is placed in a wide crucible and heated by a bunsen burner, at first gently, being constantly stirred by a stout copper wire. If this is not done, it quickly forms a hard cake, and complete combustion is impossible. After a time raise the temperature to a red-heat, and stir frequently, until the theoretical gain in weight is obtained. The heating may be finished in a small crucible furnace or a muffle. The product should be completely soluble in dilute sulphuric acid.

If copper turnings, filings, or clippings of copper wire are used, combustion will be incomplete. This, however, is immaterial for most purposes. (See p. 10).

Mercuric oxide is also prepared on the large scale by heating mercury in air under pressure. It is not, however, a useful laboratory method.

When iron wire is burnt in oxygen the oxide Fe_3O_4 is produced.

Method II.

2. **Preparation of quick-lime from marble.**—Some clean pieces of marble are placed in a crucible and heated for several hours in a crucible furnace or a muffle. The Méker furnace (Fig. 4*c*) is also excellent for this purpose. The reaction

$$CaCO_3 \rightleftarrows CaO + CO_2$$

is reversible, and unless the CO_2 formed is removed (by air current, etc.) the action will not be complete except at a very high temperature. Continue the heating until the theoretical loss of weight is obtained.

3. **Magnesium oxide** is prepared similarly from magnesite. The decomposition in this case takes place much more readily.

4. **Copper oxide.**—Weigh out convenient quantities of copper sulphate $CuSO_4, 5H_2O$, and sodium carbonate $Na_2CO_3, 10H_2O$. Dissolve them separately in water, filter if necessary, raise to a boil and mix gradually with constant stirring. A basic carbonate of copper is precipitated, which is filtered, washed with boiling water till 25 c.cs. of the filtrate no longer react with barium chloride solution (*i.e.* till the soluble sulphate is washed out), and dried in the steam oven. It is transferred to a crucible and heated strongly to convert it to the oxide.

$$\underset{249}{CuSO_4(5H_2O)} + \underset{286}{Na_2CO_3(10H_2O)} = CuCO_3 + Na_2SO_4,$$

and then $CuCO_3 + H_2O$ goes partly into $Cu(OH)_2 + CO_2$. The higher the temperature and the more dilute the solution, the more basic will be the carbonate. (See under *basic salts*.)

Thus we see that 25 gms. of copper sulphate crystals and 29 gms. of soda

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crystals are convenient quantities to take. The yield of CuO should be theoretical.

Cadmium oxide, CdO, may be prepared similarly.

5. **Barium oxide from witherite, $BaCO_3$.**—Since barium carbonate is completely decomposed by heat only with great difficulty, it is reduced by mixing with carbon and heating strongly.

$$BaCO_3 + C = BaO + 2CO.$$

Grind up very finely 50 gms. of the mineral, mix *intimately* with the theoretical weight of carbon (lamp-black should be used, as other forms of carbon leave considerable ash), place in a clay crucible and heat strongly for 2-3 hours in a muffle. Bottle up the BaO whilst still warm, and seal the cork with wax.

The BaO should dissolve in dilute hydrochloric acid without evolution of carbon dioxide. On exposure to the air it absorbs carbon dioxide and moisture very readily.

6. **Strontium oxide.**—SrO (strontia) may be similarly prepared from strontianite, $SrCO_3$.

Method III.

By strongly heating the nitrate of the metal.

7. **Copper oxide from copper.**—A known weight of copper is dissolved in the least possible amount of strong nitric acid, and the solution evaporated to dryness on a sand-bath in a good draught cupboard. Care must be taken towards the end to prevent the substance spirting.

A green basic nitrate of copper is left, which on being heated strongly decomposes, leaving CuO. However strongly this is heated, it always contains a little nitrogen (probably as a highly basic nitrate), and copper oxide prepared in this way is useless for organic combustions in which nitrogen is being determined (*q.v.*).

For such a purpose copper oxide made from wire clippings by heating them strongly in air is used.

The normal action of heat on a metallic nitrate is represented as follows:

$$2X(NO_3)_2 = 2XO + 4NO_2 + O_2.$$

This takes place more or less readily with all nitrates except those of sodium, potassium and ammonium. But the action is not always as complete as in the case of copper nitrate: *e.g.* barium nitrate requires an exceedingly high temperature to effect anything like complete decomposition.

Furthermore, lead nitrate is the only common nitrate (except silver nitrate, *q.v.*) which does not contain water of crystallisation. When such nitrates are heated, partial hydrolysis takes place during dehydration, leaving a *basic* nitrate (see under basic salts), somewhat as follows:

$$4\ Cu(NO_3)_2,6H_2O = Cu_4(OH)_6(NO_3)_2 + 6HNO_3 + 18H_2O.$$

Ferric oxide, Fe_2O_3, is prepared by the method of No. 7. (See also p. 12.)

8. **Mercuric oxide from mercury.**—A known weight of mercury is dissolved in the minimum quantity of strong nitric acid, and evaporated carefully to

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dryness. (A basic nitrate is thereby formed.) This is *cautiously* heated on a gauze, remembering that mercury oxide is readily decomposed by a high temperature. The mass gradually darkens in colour till it is almost black. This black substance is hot HgO (red when cold), and its decomposition into mercury and oxygen is detected by the condensation of mercury on a test-tube of cold water held over the basin. When this occurs, allow to cool. Compare the yield with that demanded by theory.

It should here be noted that mercurous nitrate and mercuric nitrate are both liable to be formed, but either salt when heated gives mercuric oxide, thus:

$$Hg_2(NO_3)_2 = 2HgO + 2NO_2,$$
$$2Hg(NO_3)_2 = 2HgO + 4NO_2 + O_2.$$

Note that silver oxide, Ag_2O, cannot be prepared thus, as its decomposition temperature is below that of silver nitrate. On heating silver nitrate we have:

$$2AgNO_3 = 2Ag + 2NO_2 + O_2.$$

The action of strong nitric acid on tin and antimony is to form the oxides (hydrated) directly. In the case of tin a white insoluble substance is formed, having when dried *in vacuo* the empirical formula

$$H_2SnO_3 \ (i.e.\ SnO_2 . H_2O).$$

It is called meta-stannic acid, and is quite different in its properties from the substance produced when stannic chloride is treated with ammonium hydroxide, though this substance has the same empirical formula. (For full discussion of these compounds see under Tin in Qualitative Analysis.)

9. **Stannic oxide, SnO_2.**—Five grams of tin are treated in a basin, in the draught-cupboard, with nitric acid (1 : 1). As the action slackens the liquid may be *gently* warmed, and more acid added as required until the tin is dissolved. Dilute considerably, allow to settle, decant, add boiling water, filter, wash, dry and ignite. The product should be white, but as commercial tin contains traces of lead, iron, etc., it is generally yellow as thus prepared.

The action may be represented:

$$Sn + 4HNO_3 = H_2SnO_3 + H_2O + 4NO_2.$$

Ignited SnO_2 is quite insoluble both in acids and alkalis. It has much more markedly acidic than basic properties, and is really an acid anhydride.

Antimony pentoxide, Sb_2O_5, is similarly produced, but the product must not be heated above 275° C., or Sb_2O_4 will be formed.

Method IV.

By the action of heat on the metallic hydroxide.

This method fails (for practical purposes) in the case of sodium and potassium hydroxides, but will work in all other cases. The metallic hydroxide is obtained by adding sodium hydroxide solution (the required amount only) to a solution of a salt of the metal, the precipitate is filtered, washed and dried, and heated.

If excess of alkali is used in the precipitation, it is retained in the precipitate very tenaciously. Moreover, the hydroxides of several metals are soluble in excess of alkali, *e.g.* zinc, lead, tin.

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In the case of mercury and silver salts (also gold and platinum) the hydroxides do not exist, and the oxide is therefore obtained at once, *e.g.*

$$Hg_2(NO_3)_2 + 2KOH = Hg_2O + 2KNO_3 + H_2O,$$
$$Hg(NO_3)_2 + 2KOH = HgO + 2KNO_3 + H_2O,$$
$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O.$$

Ammonium hydroxide gives a much cleaner precipitate than sodium hydroxide in the case of the trivalent metals Fe(ic), Cr, Al and Bi.

10. **Mercurous oxide, Hg_2O, from mercury.**—Treat some mercury with insufficient cold dilute nitric acid for complete solution. Add to the solution the right amount of caustic soda solution. Filter, wash and dry the black precipitate in the steam oven.

Note.—Mercuric oxide similarly prepared is *yellow*.

11. **Chromic oxide, Cr_2O_3.**—The mother-liquor from the preparation of chrome alum is treated with ammonia till alkaline and boiled for several minutes until the precipitate will settle well.

Avoid a large excess of ammonia, in which the $Cr(OH)_3$ is somewhat soluble. Filter, wash and dry the greenish-grey hydrate, and ignite strongly in a muffle furnace.

Ferric oxide, Fe_2O_3, and alumina, Al_2O_3, may be similarly prepared, the former from iron (dissolve in aqua regia, forming ferric chloride), the latter from alum.

12. **Bismuth oxide, Bi_2O_3.**—Dissolve 10 grams of bismuth nitrate, $Bi(NO_3)_3$, $5H_2O$, in as little dilute nitric acid as possible. Add a considerable excess of ammonia solution, boil for some time, filter off the hydroxide, wash, dry and heat to about 250° C. to convert to the oxide, a pale yellow powder.

If potash be added to the *boiling* nitrate solution the trioxide is precipitated at once in crystalline form.

Bi_2O_3 is also obtained by heating the carbonate or nitrate in the usual way.

13. **Crystalline litharge, PbO.**—To a boiling solution of 15 grams of caustic soda in 100 c.cs. of water add a boiling solution of lead acetate (15 grams in 75 c.cs. of water). Continue the boiling until the litharge forms a crystalline precipitate; decant, add boiling water, filter, wash with boiling water till free from alkali, and dry at 100° C.

Stronger alkali gives larger crystals of a darker colour.

V. Special Methods.

These are adopted when (*a*) they are more economical than the above; (*b*) when the above methods fail.

As an example of (*a*) may be taken the preparation of

14. **Strontia from celestite, $SrSO_4$,** which is reduced to SrS by ignition with carbon, and converted to oxide by heating with CuO.

$$SrSO_4 + 4C = SrS + 4CO,$$
$$SrS + CuO + H_2O = Sr(OH)_2 + CuS.$$

An intimate mixture of celestite with slightly more than the calculated

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amount of carbon is packed tightly into a crucible, covered with a layer of powdered carbon and heated to white heat in a suitable furnace, until a portion dissolves practically completely in dilute hydrochloric acid. It is then suspended in plenty of water, excess of commercial copper oxide added, and boiled till it no longer contains any soluble sulphide (test a portion with lead acetate). Filter whilst hot, wash the residue with a little boiling water, which is added to the main filtrate, and leave to crystallise. (Exclude air.) Filter rapidly on the pump, dry and bottle as quickly as possible.

The product is $Sr(OH)_2, 8H_2O$; it may be dehydrated by ignition if required.

Baryta may be similarly made from barytes, $BaSO_4$.

As examples of (*b*) may be taken:

Cuprous oxide, Cu_2O, which is readily converted to CuO by heat, and no soluble cuprous salt is available for the wet methods.

Ferrous, manganous and stannous oxides, which are also readily oxidised, even at ordinary temperatures. These are obtained by heating the oxalate in a current of carbon dioxide.

$$FeC_2O_4 = FeO + CO + CO_2.$$

Note also that ferric oxide, Fe_2O_3, is most economically made from ferrous sulphate, $FeSO_4, 7H_2O$, by ignition. It is thus obtained as a residue in the manufacture of Nordhausen sulphuric acid. As thus obtained it is an impalpable powder, called "jeweller's rouge." Several other preparations follow.

15. **Cuprous oxide, Cu_2O, from copper sulphate.**—25 gms. of copper sulphate and 15-20 gms. of glucose, $C_6H_{12}O_6$, are dissolved separately in water and filtered if necessary into a basin. A solution of sodium hydroxide (bench strength) is now added. The precipitated copper hydroxide dissolves in the glucose to form a blue solution. It is then heated, stirring constantly until the blue colour has entirely gone and an orange-red precipitate forms. If the blue colour persists, more caustic soda or glucose may be required. Filter, wash very thoroughly with boiling water, and dry in a steam oven.

The glucose acts as a gentle reducing agent, thus:

$$2Cu(OH)_2 - O = Cu_2(OH)_2 + H_2O$$

gluconic acid, $C_6H_{12}O_7$, being formed. The $Cu_2(OH)_2$ is dehydrated at 100° C., forming Cu_2O.

16. **Manganous oxide, MnO, from Manganous sulphate.**—To a solution of manganous sulphate a solution of potassium oxalate in requisite quantity is added. A white precipitate falls. Allow to stand for a short time, filter, wash and dry in the steam oven.

$$MnSO_4 + K_2C_2O_4 = K_2SO_4 + MnC_2O_4.$$

The perfectly dry manganous oxalate is transferred to a hard glass tube drawn out near each end, and a current of dry carbon dioxide is passed through it. When all air is displaced, the tube is heated.

$$MnC_2O_4 = MnO + CO + CO_2.$$

When the white substance has turned into an olive green powder (MnO) the tube is sealed whilst carbon dioxide is still passing through.

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On exposure to air, even at the ordinary temperature, MnO absorbs oxygen and forms higher oxides of manganese.

Ferrous oxide, FeO, is prepared from ferrous oxalate in a precisely similar way. It is a black powder.

Stannous oxide, SnO, may also be obtained thus, but stannous hydroxide, being far more stable than the oxide, may be used instead of the oxalate. It is prepared from stannous chloride in the usual way. SnO is stable at the ordinary temperature as thus prepared. It is a black powder.

17. **Chromic oxide, Cr_2O_3.**—For use as a pigment this oxide is not prepared according to No. 11, as other methods give a more brightly coloured product. Several special methods are in use, which are merely mentioned here.

(1) Heat carefully in a basin (preferably metal) a little ammonium dichromate; it decomposes violently:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O.$$

(2) An intimate mixture of potassium dichromate and ammonium chloride in the required proportions may be used instead of ammonium dichromate; in this case it is necessary to heat the mixture fairly strongly in a crucible. Boil the product with water, filter, wash, dry and ignite. Use it for preparing metallic chromium (No. 32).

(3) Mix intimately equal weights of potassium dichromate and boric acid with enough water to make a stiff paste. Transfer to a clay crucible, heat gently till dry and then fairly strongly. When cold extract with water and boil well. Filter, wash and dry. The product is a partly hydrated oxide, *Guignet's green*, $Cr_2O(OH)_4$.

18. **Antimony trioxide, Sb_2O_3.**—The first portions of the distillate in the preparation of antimony trichloride (No. 118) will contain a considerable amount of this substance, also much hydrochloric acid. On diluting it largely, partial hydrolysis takes place:

$$SbCl_3 + H_2O = SbOCl \downarrow + 2HCl.$$

Hence dilute the liquor with much *cold* water and allow to settle. Wash several times by decantation with cold water, and then suspend in much water and boil for some time. Filter, wash and dry at 200° C. A sample is boiled with sodium carbonate solution, filtered and the filtrate acidified with nitric acid and tested for a chloride. If any is present, the hydrolysis was not complete.

19. **Antimony pentoxide, Sb_2O_5.**—This is prepared similarly to arsenic pentoxide (*q.v.*) by oxidising the trioxide with strong nitric acid. When strongly heated it forms stable Sb_2O_4. Hence dry the above product at 275° C.

20. **Bismuth pentoxide, Bi_2O_5** (so-called "bismuthic acid").

(*a*) Bismuth trioxide (No. 11) is suspended in an excess of hot 30% potash solution, and chlorine is passed in, using a funnel as delivery tube (Fig. 20).

(*b*) *Or*, Some potassium chloride is added to the above suspension, and it is electrolysed in a platinum basin (made the anode).

In either case a dark-coloured insoluble deposit is produced, said to be potassium bismuthate, $KBiO_3$. Dilute the liquid considerably, decant, wash with water, and boil the powder with strong nitric acid for a *short* time.

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Bismuthic acid, $HBiO_3$, is produced, a scarlet powder; dilute the liquid, decant, filter, wash and dry at 100° C. Oxygen is evolved if the heating is continued beyond the time necessary to drive off the "hydrate" water.

Heated very strongly, it passes into Bi_2O_4 (?).

B. PEROXIDES.

A metallic peroxide is one which

(*a*) When heated gives off oxygen and leaves a lower oxide.

(*b*) When treated with hot hydrochloric acid gives off either chlorine or oxygen.

(*c*) When heated with strong sulphuric acid gives off oxygen.

There are two general methods of preparation:

(i) The dry method, in which the lower oxide is heated in air or with a suitable oxidising agent and thus made to take up oxygen.

(ii) The wet method, in which the hydroxide of the lower oxide is precipitated by an alkali and then oxidised by a solution of an oxidising agent.

Examples of the Dry Method.

21. **Barium peroxide, BaO_2.**—Barium monoxide, BaO, from No. 5, is placed in a hard glass tube and heated to dull redness in a slow stream of oxygen which is dried by strong sulphuric acid and passed over soda-lime to absorb any carbon dioxide. The process is continued till the gain in weight is approximately that demanded by the equation

$$2BaO + O_2 \rightleftarrows 2BaO_2.$$

Air may be used, but the process will take considerably longer.

The product may be used for the preparation of hydrogen peroxide (No. 27).

When BaO_2 is heated to a bright red heat the above reaction goes from right to left.

The method forms the basis of Brin's process for obtaining oxygen from the air.

22. **Red lead, Pb_3O_4.**—This may be obtained by heating litharge to 350°-400° C. in air or oxygen, either in a similar manner to that of No. 17, or by spreading the litharge on a clean sand-tray and heating with a rose-burner. In either case the operation is lengthy, and the regulation of temperature difficult. A small quantity may be conveniently prepared by weighing out litharge and potassium chlorate in the proportion $3PbO : KClO_3$. The chlorate is dissolved in the minimum of water, and the litharge made into a paste with the solution. It is then dried carefully and heated to a temperature of 400°-450° (*no higher*). When the action is complete allow to cool, grind up the mass, extract with boiling water, and finally filter, wash and dry at 100°.

23. **Lead peroxide, PbO_2** (Kassner, *Chemische Industrie*, **13**, 104, 120).—When a mixture of litharge and calcium carbonate are heated in air, the reaction

$$PbO + 2CaCO_3 + O_2 = Ca_2PbO_4 + 2CO_2$$

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takes place, calcium plumbate being formed. This is decomposed by nitric acid thus:

$$Ca_2PbO_4 + 4HNO_3 = 2Ca(NO_3)_2 + PbO_2.$$

Hence mix intimately litharge and precipitated calcium carbonate in the proportions demanded by the equation, put into a clay crucible and ignite strongly in a furnace, allowing free access of air, and stirring frequently with a stout iron wire. The ignition is continued until a small sample of the product gives no test for carbonate. Allow to cool, and slowly add the powdered mass to a slight excess of hot dilute nitric acid kept hot in a large basin. Decant and treat the residue with more boiling dilute nitric acid. Finally filter, wash and dry the dark-brown oxide, and dry at 120° C. in an air-oven.

Examples of the Wet Method.

24. **Lead peroxide.**—If lead hydroxide be precipitated from a solution of a lead salt, and treated with an oxidising agent such as hypochlorite, hydrogen peroxide, chlorine, etc., it is oxidised to lead dioxide.

The most suitable oxidising agent is bleaching powder, which contains the necessary alkali as well as the oxidising agent.

To a solution of 50 grams of lead acetate kept hot in a large basin, add gradually a filtered solution of bleaching powder, until a specimen of the clear liquid, treated with bleaching solution and heated, gives no more precipitate.

$$Pb(C_2H_3O_2)_2 + Ca(OH)_2 = Pb(OH)_2 + Ca(C_2H_3O_2)_2,$$
$$Pb(OH)_2 + CaOCl_2 = CaCl_2 + PbO_2 + H_2O.$$

Then allow to settle, decant, wash twice by decantation with hot water, then once with hot water containing a little nitric acid. Filter, wash and dry at 120° C. in air oven.

25. **Lead sesqui-oxide, Pb_2O_3.**—This oxide is obtained by the oxidation of a strongly alkaline lead solution.

To a solution of 50 grams of lead acetate in 250 c.cs. of water in a large basin add 10% caustic soda solution, gently warming meanwhile, till the precipitate formed at first redissolves. Then add a solution of bleaching powder, freshly made by grinding bleaching powder in a large mortar with cold water and filtering. The liquid is heated meanwhile, and the hypochlorite solution slowly added until no more precipitate forms. Allow to settle, decant *at once*, wash with boiling water by decantation, filter, wash and dry at 100°. An orange powder.

N.B.—Unless the washing from excess of bleaching solution is done at once, atmospheric carbon dioxide will soon precipitate calcium carbonate, from which the Pb_2O_3 cannot be freed. It is therefore better, though not so economical, to use *sodium* hypochlorite solution.

The action of dilute nitric acid on Pb_2O_3 and Pb_3O_4 is as follows:

$$Pb_2O_3 + 2HNO_3 = Pb(NO_3)_2 + PbO_2 + H_2O.$$
$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O,$$

thus indicating that they are both salts of plumbic acid.

Pb_2O_3 is lead meta-plumbate (*i.e.* from H_2PbO_3).
Pb_3O_4 is lead ortho-plumbate (*i.e.* from H_4PbO_4).

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Acetic acid acts similarly to nitric.

26. **Barium peroxide (hydrated), $BaO_2,8H_2O$.**—50 grams of the crude barium peroxide from No. 21 are ground with water to a thin cream, cooled to 0° C., and added slowly to the calculated amount of ice-cold dilute hydrochloric acid (about 2 N) until present in *slight* excess. Filter (or decant) and pour into it a saturated barium hydroxide solution at 0° C. until no more precipitate forms. Filter the crystalline mass on the pump, wash with *several small* quantities of ice-water, and dry at 130° C., at which temperature the water of crystallisation is lost.

Reactions:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2,$$
$$Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O.$$

The BaO_2 then crystallises with $8H_2O$, forming most probably

$$Ba(OH)_4 . 6H_2O.$$

27. **Hydrogen peroxide, H_2O_2.**—Crude BaO_2 from No. 21 is added a little at a time to 5% phosphoric acid solution cooled with ice and contained in a mortar. Grind thoroughly and continue the addition and grinding until the reaction to litmus is neutral. Allow to settle and decant the liquid as far as possible from the insoluble barium phosphate. Extract the residue once or twice with a little ice cold water and add the extractions to the main portion. Finally filter the decanted liquids. The strength may be found by titration with permanganate (Quantitative Analysis, p. 249), or by measuring the oxygen evolved when the peroxide is catalytically decomposed by MnO_2 (p. 276).

The solution may be concentrated by evaporation at 75° C. in a *perfectly smooth* basin, till evolution of oxygen commences. Further concentration must be performed by vacuum distillation (p. 285).

The pure liquid is dangerous to handle owing to its liability to explosive decomposition.

For the reactions of H_2O_2 see p. 116.

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CHAPTER IV.

METALS.

METALS are obtained from either their oxides or sulphides by the following methods:

1. Reduction of the oxide by heating with a reducing agent such as hydrogen, carbon monoxide, carbon, potassium cyanide, or another metal, as aluminium or magnesium.

2. Reduction of the sulphide by means of iron or aluminium.

N.B.—" Auto-reduction " as practised on the large scale by roasting two-thirds to oxide and then heating, is not a practical laboratory method.

3. Reducing agents in solution.

EXAMPLES OF METHOD 1.

28. **Copper from copper oxide.**—Porous lumps of copper oxide made from the nitrate are packed in a hard glass tube and heated in the tube furnace, whilst a stream of dry hydrogen made from a pure zinc-copper couple and sulphuric acid is led over it. (Carbon monoxide is preferable, as being purer.) Note that all air must be swept out of the apparatus by the hydrogen stream before the tube is heated, or an explosion will result. The copper is obtained in pink porous lumps, and in this condition is readily oxidised by exposure to air. It should be cooled in the hydrogen stream and bottled at once.

Iron (" ferrum redactum "), nickel and cobalt may be similarly prepared. Nickel as thus made is of great importance as a catalyst.

29. **Pure lead, according to Stas.**—Pure lead carbonate is added gradually to some molten potassium cyanide (excess) in a crucible.

$$PbCO_3 = PbO + CO_2 \uparrow$$
$$PbO + KCN = KCNO + Pb.$$

The lead thus obtained is re-melted with pure potassium cyanide; it should exhibit when molten a convex surface as brilliant as that of mercury. It is very soft and tarnishes rapidly in the air.

The pure lead carbonate is prepared thus: 50 grams lead acetate dissolved in warm water are digested with thin lead-foil at 50° C. (This removes traces of less positive metals, as copper.) The filtered solution is poured into almost boiling dilute sulphuric acid. The lead sulphate is washed by decantation till free from sulphuric acid, suspended in water and treated with a solution of ammonium carbonate and ammonia at about 35° C., whereby it

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is converted into lead carbonate. It is again washed thoroughly by decantation, but still contains traces of iron. To remove this a portion is heated carefully till converted into litharge, and the rest dissolved in dilute nitric acid (strength 2N), leaving a little undissolved. This lead nitrate solution is boiled and the litharge gradually added.

$$2Fe(NO_3)_3 + 3PbO + 3H_2O = 3Pb(NO_3)_2 + 2Fe(OH)_3.$$

The solution is filtered into excess of ammonium carbonate solution, and the precipitate thoroughly washed and dried. It is now ready for use. (See Stas' first *Memoir* (1860).)

For ordinary purposes, lead may be obtained from commercial litharge by mixing with the requisite weight of carbon (wood-charcoal) and some fusion mixture to act as a flux.

$$PbO + C = CO + Pb,$$

and heating in a plumbago crucible in a furnace.

The mixture should be stirred occasionally with the stem of a clay pipe, to cause the lead buttons to run together. Granulate the fused metal by pouring it slowly from a height of 4 feet into a *large* bowl of cold water.

30. **Tin from stannic oxide, SnO_2.**—Either commercial stannic oxide or the mineral *tinstone* may be used. If the latter, it must be finely powdered. Mix equal weights of the oxide and potassium cyanide, place in a porcelain crucible, and heat strongly in a furnace until a clean button of molten tin can be seen under the fused residue.

$$2KCN + SnO_2 = 2KCNO + Sn.$$

Allow to cool and place the crucible in warm water in a basin; the mass readily dissolves and the button is washed and dried.

SnO_2 may also be reduced by hydrogen, as in No. 28.

Antimony may be prepared in a similar manner from some of the antimony trioxide from No. 18, using a slight excess of potassium cyanide.

So also may **lead** and **bismuth** be prepared from their oxides.

Reductions by other Metals.

A. **By Aluminum.** (Goldschmidt, *Liebigs Ann.*, **301**, 19 (1899).)

N.B.—Do not attempt these on too small a scale. They are best performed out of doors.

31. **Iron from iron oxide** (the original "thermite").—A mixture of magnetic oxide (Fe_3O_4, hammer scale) and aluminium filings (not powder) in the right proportions is placed in a crucible, and a small hole made in the top of the mixture. Into this is introduced a "fuse" consisting of a mixture of barium peroxide and magnesium powder in the correct proportions. A piece of magnesium ribbon is placed in this, the crucible is set in a larger crucible, and the magnesium lighted. A violent reaction starts, the whole mass becomes incandescent, and the iron produced melts and runs to the bottom of the crucible and is there protected by the fused alumina.

$$3Fe_3O_4 + 8Al = 4Al_2O_3 + 9Fe.$$

The method is used for welding tram-lines; the molten iron is allowed

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to run into a suitable mould placed round the ends to be welded, and it forms a solid joint.

Metallic manganese is made similarly from Mn_3O_4 (got by heating pyrolusite very strongly in a crucible furnace) and aluminium. The heat is insufficient to fuse the manganese completely.

32. **Chromium from chromic oxide.**—In this case the heat of the reaction is hardly sufficient to melt the chromium completely, so the temperature is increased either by heating the crucible in a furnace till the reaction starts, or more simply by mixing some dry potassium dichromate with the chromic oxide, whereby the heat of the reaction is increased.

Some potassium dichromate is just melted in a porcelain basin and allowed to cool. It can then be reduced easily to a fine powder, 20 grams of which are mixed with 70 grams of absolutely dry chromic oxide (from No. 11), and sufficient aluminium filings to reduce the chromic oxide only. The mixture is placed in a clay crucible of 200 grams capacity, which is packed in dry sand in a flower-pot or some such vessel.

Some of the fuse mixture (see No. 31) is placed in a small hole in the reaction mixture, and a piece of magnesium ribbon is fixed therein and lighted. The chromium produced may not be completely melted; the partly fused regulus may be used for the preparation of chromic chloride (No. 117).

Silicon and boron may also be made by a modification of the thermite process. (See under Non-metallic elements.)

2. Reduction of a Sulphide by Metallic Iron.

33. **Antimony from Stibnite, Sb_2S_3.**—20 grams of finely powdered stibnite are mixed intimately with rather less than the calculated quantity of fine sifted iron filings, 2 or 3 grams of anhydrous sodium sulphate to act as a flux and a pinch or two of powdered wood charcoal to prevent oxidation. The mixture is put into a porcelain crucible provided with a lid, and heated to a medium red-heat in a suitable furnace.

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb.$$

The products should just fuse, when the antimony will collect at the bottom of the crucible. It is often unnecessary to break the crucible, as a sharp tap will detach the mass when cold.

The antimony may be freed from adhering bits of iron sulphide by treatment with dilute hydrochloric acid.

If more than the required amount of iron is used, some of it will alloy with the antimony. Hence use a slight defect of iron, as the stibnite is probably not quite pure.

Lead may be similarly obtained from galena, PbS, and bismuth from bismuth glance, Bi_2S_3.

3. Wet Methods.

34. **Silver from coins or scrap silver, according to Stas.**—Dissolve a known weight of silver-copper alloy in excess of boiling dilute nitric acid, evaporate dry, and heat *very carefully* till the nitrates just fuse. Break up the mass and leave it for 48 hours with excess of ammonia solution. Then filter, wash the

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residue with ammonia, and add the washing to the filtrate, and finally dilute to such a volume that it contains 2°/₀ (or less) of silver.

Sulphur dioxide is then passed into the liquid (with cooling) until a test portion decolorises when boiled. The cold liquid is covered and left for 48 hours. About a third of the silver *crystallises* out. Decant the blue liquid and heat it to 70° C., which completes the reduction at once. Wash the silver powder so produced by decantation, leave under ammonia for several days, and dry it, mix it with an equal bulk of anhydrous borax, and fuse on a cupel by the blowpipe. Stas speaks very highly of this silver.

35. **Silver from the laboratory residues.**—The residues, consisting of silver halides, are reduced by boiling with caustic soda and glucose solution.

$$2AgCl + 2NaOH = Ag_2O + 2NaCl + H_2O$$

$$Ag_2O - O \text{ (by glucose)} = 2Ag.$$

Shake the residues with hot water, allow to settle, decant, repeat several times, finally pour the whole into a large basin and add caustic soda solution and glucose. Keep the liquid simmering gently, adding fresh caustic soda and glucose as required, until a portion of the powder, when thoroughly washed, dissolves up clear in hot dilute nitric acid (*i.e.* the halides are completely reduced). Then decant, wash thoroughly, and treat as in No. 34.

36. **Platinum from residues.**—The residues, consisting of various salts of H_2PtCl_6, are evaporated dry on a water-bath, extracted with hot water, filtered and poured into warm concentrated sodium hydroxide solution containing a little glycerine. The precipitate is allowed to settle, washed once by decantation, filtered through an ashless filter and ignited strongly. It is then converted into hydrochlorplatinic acid by solution in 'aqua regia.' (Any insoluble residue here is iridium.) The solution is then precipitated by adding concentrated ammonium chloride and alcohol, the precipitate dried and ignited strongly in a porcelain crucible.

$$(NH_4)_2PtCl_6 = 2NH_4Cl + Pt + 2Cl_2.$$

The product is weighed and again dissolved in aqua regia, diluted and evaporated with frequent additions of small quantities of hydrochloric acid, and later of a little chlorine water to oxidise platinous compounds to the platinic state. It is finally evaporated on the water-bath to a thick syrup and diluted to a known volume with water.

37. **Gold from scrap metal.**—Dissolve in aqua regia, evaporate, dilute, filter from silver chloride and reduce by boiling with ferrous sulphate solution.

Decant, heat with dilute hydrochloric acid, filter on an ashless filter, wash thoroughly, first with dilute hydrochloric acid, then with water, dry and ignite. Convert it to $HAuCl_4$ (hydro-chlorauric acid) by careful solution in aqua regia as for platinum above.

Special Case.

38. **Mercury** may be obtained by heating compounds of mercury with quick-lime,

$$2CaO + 2Hg_2Cl_2 = 2CaCl_2 + 4Hg + O_2,$$

in a hard glass tube whose drawn-out end dips under water in a beaker. For further details see under Mercury in 'Quantitative Analysis.'

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CHAPTER V.

SALTS.

SALTS are classified as:

A. **Normal salts,** in which the hydrogen of the acid is completely replaced by a metal or positive radical.

B. **Acid salts,** in which hydrogen forms at least one of the positive radicals.

C. **Basic salts,** in which hydroxyl forms at least one of the negative radicals. (If two hydroxyls are present they frequently eliminate water between them, leaving oxygen as one of the negative radicals. *Cf.* SbOCl.)

D. **Double salts,** in which, broadly speaking, there are two or more different metallic or positive radicals exclusive of hydrogen. These are discussed fully below.

A. Soluble normal salts are prepared by treating the acid with

(*a*) The metal. This is of limited application.

(*b*) The metallic (basic) oxide, hydroxide, or carbonate.

(*c*) By double decomposition.

(*b*) is generally available. The determination of the neutral point by means of indicators, however, is often impossible because of the hydrolytic action of water on salts, of weak acids or bases, thus:

$$KCN + H_2O \rightleftharpoons KOH + HCN$$

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl.$$

When hydrolysis does take place, even to an extent imperceptible to the eye, the solution will react acid or alkaline according to the relative effects of the free acid or base on the indicator. This, of course, depends on the respective concentrations of the hydrion or hydroxylion; *i.e.* on whether the free acid or the free base is the more strongly dissociated under the conditions.

Thus, in the above cases, the free potash existing in a solution of potassium cyanide is strongly ionised, whereas the free prussic acid is hardly dissociated at all; hence the solution reacts alkaline to indicators. A solution of ferric chloride, on the other hand, reacts acid, for the opposite reason. In the case of very weak bases as antimony, bismuth, the mercury salts, etc., it is impossible to dissolve the salts in pure water without getting a *precipitate* of a basic salt; in which case the solution must be made in the dilute acid of which the substance is a salt. In this case hydrolysis is prevented in accordance with the law of mass action, by the presence of excess of the acid ions.

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Generally speaking (though there are exceptions) it may be taken that salts of potassium, sodium, etc., barium, strontium, calcium, magnesium, etc., and ammonium, with hydrochloric, sulphuric, nitric, and the stronger organic acids as oxalic, tartaric, citric, acetic, etc., are neutral to litmus.

But it does not follow that a salt which is neutral to litmus is neutral to other indicators. (*Cf.* sodium bicarbonate and the sodium hydrogen phosphates to phenol-phthalein and methyl orange.)

The above considerations modify the procedure in the preparation of various salts as described in the following pages.

(*a*) Preparation of salts by the action of the acid on the metal.

Most nitrates may be made thus, also the sulphates and chlorides of zinc and iron, by the action of the metal on dilute acid, and copper sulphate by the action of the metal on the strong acid.

In the cases where dilute acid is used, the metal is treated with the acid until the acid is as far as possible neutralised, the solution is filtered and concentrated.

39. **Ferrous sulphate, $FeSO_4,7H_2O$, from iron.**—A solution of this salt is rapidly oxidised when hot by atmospheric oxygen, forming an insoluble basic ferric sulphate, *e.g.*

$$2FeSO_4 + H_2O + O = 2Fe(OH)SO_4,$$

and it is therefore impossible to concentrate a solution of this salt by boiling, after the iron has been filtered off. Hence use sulphuric acid of such strength that the salt crystallises on cooling the hot solution.

To 100 c.cs. of water in a large basin add carefully 25 c.cs. of strong sulphuric acid, and then iron filings, small quantities at a time, till present in some excess (calculate). Keep the solution at about 90° C., adding water to keep up the volume, till effervescence has almost ceased. Then raise to a boil and filter through a funnel kept hot in the funnel heater, into a basin floating in cold water. Filter on the pump, drain there as far as possible, wrap in filter paper and place under a weight overnight. Do not expose unduly to the air.

40. **Copper sulphate, $CuSO_4,5H_2O$, from copper.**—Copper wool (or fine turnings), 2 parts, is added to pure sulphuric acid, 9 parts, in a flask, and heated till most of the copper has gone into solution. The evolved sulphur dioxide should be used in some other preparation (*e.g.* chrome alum) if the quantities taken give a considerable amount of this gas.

Allow the solution to get quite cold, when the copper sulphate crystallises as the monohydrate $CuSO_4$, H_2O. Carefully decant the liquid, and add the residue to 5 parts of water. Raise to boiling, filter hot and cool rapidly with stirring.

As thus prepared, unless the copper used is very pure, it will contain ferrous sulphate, with which it forms mixed crystals (monoclinic) $(Fe, Cu)SO_4$, $7H_2O$. If required pure, it is therefore dissolved in hot water, and a few c.cs. of strong nitric acid and some sulphuric acid added to oxidise the iron to ferric sulphate. The solution is then cooled, and the product recrystallised till free from nitrate. No precipitate should be obtained when excess of

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ammonia is added to the solution. (See also under zinc and manganous sulphates for method of freeing salts from iron.)

41. **Zinc sulphate, $ZnSO_4$, $7H_2O$, from hydrogen residues.**—The zinc sulphate should be freed from iron by oxidising hot with a few c.cs. of nitric acid, and the addition of sufficient zinc oxide to cause the hydrolysis of the ferric salt when well boiled.

$$Fe_2(SO_4)_3 + 3ZnO + 3H_2O = 3ZnSO_4 + 2Fe(OH)_3.$$

Filter and crystallise several times. A test portion should give a pure white precipitate, ZnS, with ammonium sulphide.

42. **Silver nitrate, $AgNO_3$.**—Pure silver (No. 34) is dissolved in some excess of dilute nitric acid (1 : 2) in a conical flask, which has a funnel resting in the neck to prevent mechanical loss. When solution is complete, the funnel is rinsed with distilled water, and the contents of the flask are transferred to a clean porcelain basin and evaporated dry on a water-bath, protected from dust by a funnel (Fig. 8). The residue is dissolved in distilled water and again dried. It is then dissolved in a minimum of hot distilled water and allowed to crystallise. Drain off the mother-liquor and dilute it to the required volume for use as a bench-reagent. The crystals are dried in a desiccator. They should not be dried with filter-paper, as in the presence of organic matter the salt is affected by light.

Solubility of silver nitrate at 15° C. = 185 (approximately).

43. **Copper nitrate $Cu(NO_3)_2$, $6H_2O$, from nitric oxide residues.**—Evaporate the residues in a draught cupboard until a test portion when cooled and stirred vigorously crystallises to a thick paste. Leave overnight to cool. Drain off the mother liquor, dissolve in the minimum of hot water, and cool below 25° C. Any crystals forming above this temperature will be the tri-hydrate.

44. **Bismuth nitrate, $Bi(NO_3)_3$,$5H_2O$.**—Pulverise commercial bismuth, dissolve in a minimum of hot nitric acid (1 : 1) and dilute considerably with water containing caustic soda (one-fifth of the weight of bismuth). Boil well, allow to settle, decant, wash and dissolve the bismuth oxide in hot nitric acid (1 : 1½), using more acid than is necessary to dissolve it. Evaporate to crystallisation, with addition of more acid should any basic nitrate form.

The treatment with caustic soda removes oxides of arsenic and antimony, which elements commercial bismuth usually contains.

Should the solution of nitrate require filtering, an asbestos filter is necessary.

45. **Lead nitrate, $Pb(NO_3)_2$, from lead.**—Hot *dilute* nitric acid should be used, the excess evaporated off, and the salt recrystallised from water. Many specimens of lead contain tin; if so, meta-stannic acid (insoluble) will be formed by the action of the acid, and is filtered off before the recrystallisation.

46. **Stannous chloride, $SnCl_2$,$2H_2O$.**—100 gms. of tin are treated with 200 c.cs. of strong hydrochloric acid and 25 c.cs. of water in a large flask. If the action becomes too vigorous, cool by immersion in water.

When the action is over (there should be some undissolved tin left) filter through glass-wool into a conical flask, cork and set aside to crystallise. Drain and dry in the usual way.

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47. **Zinc chloride, $ZnCl_2$.**—Dissolve zinc in hydrochloric acid, evaporate to dryness with care, and just fuse the product. Allow to cool, detach from basin by gently warming, and bottle at once. Do not touch it with the fingers.

(*b*) From base or carbonate and acid.

The salts of sodium, potassium and ammonium, barium, strontium and calcium enumerated above can be prepared (if they are soluble in water) by adding the hydroxide (dissolved if soluble) to the acid till neutral to litmus paper. Sodium or potassium carbonates may be similarly used, if the solutions are kept hot, to drive off carbon dioxide, which affects the litmus. If the base or carbonate is insoluble in water, add it gradually to the hot dilute acid till in slight excess. Boil, filter and crystallise.

The student should now be able to prepare most normal salts of common acids and bases, without further instructions. A few special cases where there is difficulty with the indicator are given under '*acid salts*.'

48. **Barium chloride, $BaCl_2,2H_2O$,** from **witherite, $BaCO_3$.**—Coarsely powdered witherite is added slowly to 300 c.cs. of hot dilute (1 : 1½) hydrochloric acid till effervescence ceases. 20 grams of the *finely* powdered mineral are now added, and the solution boiled for some time. This hydrolyses ferric chloride, as iron is present in practically all minerals.

$$2FeCl_3 + 3H_2O + 6BaCO_3 = 2Fe(OH)_3 + 6BaCl_2 + 6CO_2.$$

Filter hot, evaporate to crystallisation, obtain a further crop from the liquor, add the two crops together and recrystallise, allowing the hot solution to cool slowly to obtain larger crystals. Use the mother liquors for No. 50.

Strontium chloride, $SrCl_2,6H_2O$, is similarly made from strontianite, $SrCO_3$.

Calcium chloride, $CaCl_2,6H_2O$, for use in freezing mixture, is similarly made from the liquors of the carbon dioxide 'Kipp.'

49. **Potassium chromate, K_2CrO_4.**—Instead of using chromic acid it is cheaper to use potassium dichromate.

$$K_2Cr_2O_7 + K_2CO_3 = 2K_2CrO_4 + CO_2.$$

Weigh out reacting proportions, dissolve separately and mix the solutions slowly. Boil to crystallisation and cool quickly. If larger crystals are desired, a *slight* smear of vaseline should be put round the inside of the vessel just above the liquid level, as the solution 'creeps' badly.

Battery chromic acid may be used, but it contains much sulphuric acid, and potassium sulphate and chromate are isomorphous, and hence cannot be separated. The dichromate must therefore first be prepared.

(*c*) Insoluble salts.

These are *always* made by double decomposition, and *never* by treating the base or carbonate with the acid. Choose a soluble salt of both metal and acid required, and mix the solutions, generally at the boil, as the precipitates obtained at high temperatures are generally far easier to filter. Exceptions to this are of course precipitates which would be affected by heat, *e.g.* SbOCl.

N.B.—Solutions of reagents should not be too strong, or the precipitate

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will carry down with it much of the soluble substances, which cannot be removed by washing.

50. **Barium sulphate, $BaSO_4$.**—Dilute the mother liquors from the preparation of barium chloride (No. 48), raise to the boil, and add slowly to some boiling dilute sulphuric acid till no more precipitate falls. Decant, transfer to a filter, wash with boiling water, and dry in steam oven.

51. **Calcium sulphate, $CaSO_4,2H_2O$** is obtained when the liquor from the carbon dioxide 'Kipp' is diluted and treated with cold dilute sulphuric acid. Filter on the pump, wash with cold water, and dry by wrapping in filter paper.

52. **Calcium oxalate, CaC_2O_4,** is obtained when a boiling solution of pure calcium chloride is treated with a boiling solution of pure ammonium oxalate, added *gradually*. Filter, wash and dry at 100° C.

53. **Lead chromate, $PbCrO_4$ (Chrome yellow).**—Calculate the weights of lead acetate and potassium dichromate which react:

$$2Pb(C_2H_3O_2)_2, 3H_2O + K_2Cr_2O_7 = 2PbCrO_4 + 2K(C_2H_3O_2) + 2C_2H_4O_2 + 2H_2O.$$

Dissolve separately, heat and filter into the same vessel. Filter, wash and dry at 110° C.

Lead chromate is insoluble in acetic acid, which is liberated in the above reaction, but if lead nitrate be used, nitric acid is liberated in quantity sufficient to dissolve half the lead chromate.

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2KNO_3 + 2HNO_3.$$

If lead nitrate is used, therefore, ammonia is added to the mixed liquids till neutral to litmus, thus precipitating that portion of the chromate kept in solution.

54. **Barium chromate, $BaCrO_4$** (Lemon yellow), is obtained from barium chloride and potassium dichromate in a precisely similar way (mix the *boiling* solutions gradually) and subject to the same considerations as above.

Potassium dichromate is used in both cases as being far cheaper than the chromate.

55. **Lead chloride, $PbCl_2$.**—To a solution of lead acetate or nitrate add cold dilute hydrochloric acid till no more precipitate falls. Allow to settle. Wash several times by decantation, then dissolve in the minimum of boiling water and leave overnight to crystallise. The bromide and iodide are prepared in a precisely similar manner, using potassium bromide or iodide (mother-liquors from preparations of these). They are beautifully crystalline as thus prepared.

56. **Special case of double decomposition. Potassium nitrate from Chili saltpetre.**

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Weigh out molecular quantities of the reagents. Turn up the solubility curves of salt and saltpetre, and from a study of these decide how much water to take, and at what temperature, to obtain the best yield of potassium nitrate. It should be recrystallised till free from chloride.

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(*d*) Preparation of a salt from another salt of the same metal.

57. **Copper acetate, $Cu(CH_3CO_2)_2,H_2O$ from copper sulphate.**—Weigh out molecular proportions of copper sulphate and sodium carbonate; dissolve them separately, mix the solutions gradually, and raise to a boil. A *basic* carbonate of copper is precipitated, which is washed well and added to warm dilute acetic acid till no more will dissolve. Filter if necessary (or better, add a little more acetic acid) and evaporate to crystallisation. Set aside to cool.

This method is a general one. The carbonate of the metal is precipitated, washed and dissolved in the required acid.

B. ACID SALTS.

The general methods consist in

I. Mixing the required amounts of base and acid,

$$KOH + H_2SO_4 = KHSO_4 + H_2O.$$

II. Mixing theoretical quantities of normal salt and acid,

$$K_2SO_4 + H_2SO_4 = 2KHSO_4.$$

The theoretical quantities are rarely *weighed* out, for obvious reasons; volumetric measurements (which need not be scrupulously accurate) are made instead. The following examples will explain the methods adopted.

58. **Potassium hydrogen sulphate, $KHSO_4$.**—Take two equal volumes of dilute (1 : 4) sulphuric acid, neutralise one with potash or potassium carbonate (litmus) and mix with the other. Crystallise as usual.

$$K_2CO_3 + H_2SO_4 = K_2SO_4 + H_2O + CO_2,$$
$$K_2SO_4 + H_2SO_4 = 2KHSO_4.$$

59. **The orthophosphates of sodium.**—NaH_2PO_4, H_2O.
Na_2HPO_4, $12H_2O$.
Na_3PO_4, $12H_2O$.

Of these, the mono-hydrogen salt is approximately neutral to litmus. It is therefore prepared thus:

Glacial phosphoric acid (HPO_3) is dissolved in water and boiled for at least 30 minutes to convert it into H_3PO_4. A measured volume is put into a porcelain basin, a piece of litmus paper added, and then caustic soda solution is run in from a graduated cylinder till the liquid is just alkaline.

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O.$$

If the di-hydrogen salt is desired, another equal volume of the orthophosphoric acid is added to the above.

$$H_3PO_4 + Na_2HPO_4 = 2NaH_2PO_4.$$

If the normal salt is required, half as much more caustic soda is added to the neutral liquid as was required to neutralise it.

$$Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O.$$

These volume relations are clearly seen from the equations.

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Some difficulty may be experienced in crystallising these salts, especially NaH_2PO_4,H_2O, which is very soluble. The solution should be boiled down considerably, cooled and set aside with a small fragment of the solid taken from the stock-bottle. The same process assists the mono-hydrogen salt to crystallise. The normal salt solution should be concentrated considerably, cooled and thoroughly stirred with a glass rod; crystallisation then readily takes place quite suddenly. The salt has a *strongly* alkaline reaction and hence is acted on by carbon dioxide.

From the above considerations it is clear that the ion HPO_4'' is scarcely dissociated, whereas the ion H_2PO_4' dissociates into $H^{\cdot} + HPO_4''$.

60. **Sodium bisulphite, $NaHSO_3$.**—Here the neutral point lies between the acid and the normal salt, the former being strongly acid, the latter alkaline to litmus. Hence take a *strong* solution of caustic soda (or carbonate) and saturate with sulphur dioxide (cool the beaker thoroughly) till no more is absorbed. The gas is conveniently delivered from a syphon of the liquefied substance. $NaHSO_3$ will crystallise out if the solution is sufficiently concentrated; otherwise it cannot be evaporated for obvious reasons. Drain thoroughly on the pump, wrap in filter paper and place under a weight.

If the normal salt is desired, a volume of the same caustic soda solution equal to that first taken is added to the hot solution of the acid salt, and the whole cooled in a covered vessel, as the hot solution soon absorbs oxygen, forming the sulphate.

Reactions:

$$NaOH + H_2O + SO_2 = NaHSO_3,$$
$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O.$$

Preserve the mother liquor for the preparation of sodium thio-sulphate, No. 162.

The solubility of Na_2SO_3 at ordinary temperatures is about 22; the strength of the soda solution used in its preparation should therefore be calculated so that a large portion of the sulphite crystallises when the hot solution is cooled.

The sulphides of sodium, etc., are similarly prepared.

61. **Potassium "quadroxalate," $KHC_2O_4,H_2C_2O_4,2H_2O$.**—Potassium binoxalate combines with another molecule of oxalic acid, forming the well-known "salts of sorrel."

Measure out 100 c.cs. of a cold saturated solution of oxalic acid. Neutralise it with potash solution (litmus). Add 300 c.cs. more of the oxalic acid solution and crystallise.

62. **Potassium "bi-iodate," KIO_3,HIO_3.**—Weigh out the required quantities of KIO_3 and $HIO_3,2H_2O$, obtained from Nos. 129 and 97; dissolve them in a little hot water and cool quickly.

This substance is used for the standardisation of thiosulphate (see Volumetric analysis).

63. **Potassium bitartrate (Cream of Tartar), $KH(C_4H_4O_6)$.**—To a solution of potash add tartaric acid solution from a graduated cylinder till neutral to litmus. Raise to a boil and add another equal quantity of tartaric acid solution. Allow to cool.

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C. BASIC SALTS.

The general methods are:

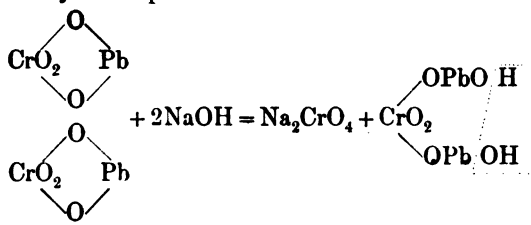
1. Partial hydrolysis of the normal salt by treatment with water or dilute alkali.

2. Treatment of the normal salt with the required quantity of the base.

64. **Basic lead chromate, Pb_2OCrO_4 (Chrome red).**—A quantity of lead chromate is boiled with *dilute* caustic soda solution sufficient to turn half the chromate to hydrate, thus:

$$2PbCrO_4 + 2NaOH = Pb(OH)_2 + PbCrO_4 + Na_2CrO_4.$$

What actually takes place is:



65. **Antimony oxychloride, $Sb_4O_5Cl_2$ (powder of Algaroth).**—Pour a solution of antimony trichloride in a little hydrochloric acid into a large volume of hot water. Wash by decantation and dry.

It should be soluble in carbon disulphide and in chloroform. (Use the first runnings of No. 118 for this experiment.)

BiOCl is similarly obtained from bismuth chloride.

66. **Bismuth "sub-nitrate," $Bi(OH)_2NO_3$.**—10 grams of bismuth nitrate crystals (No. 44) are well ground in a mortar with cold water and poured into 200 c.cs. of boiling water in a basin. Allow to settle, wash by decantation, filter, wash and dry at 30° C.

67. **Bismuth carbonate, $Bi_2(OH)_4CO_3$** is prepared by adding sodium bicarbonate solution to a bismuth salt. Both the latter basic salts of bismuth are used in medicine for indigestion, etc.

68. **Basic lead acetate, $Pb_2(OH)_2(C_2H_3O_2)_2$.**—Obtained by dissolving the correct amount of litharge in a hot *strong* solution of lead acetate. It should be cooled out of contact with air, when the basic acetate will crystallise out. The filtrate should be used for the preparation of

69. **Basic lead carbonate (White lead), $Pb_3(OH)_2(CO_3)_2$,** which is obtained by passing carbon dioxide into the solution of basic lead acetate.

$$2CO_2 + 2Pb_2(OH)_2(C_2H_3O_2) = Pb(OH)_2, 2PbCO_3 + Pb(C_2H_3O_2)_2.$$

Various methods of preparing this valuable pigment are in use; that of *Milner* may be mentioned, which consists in grinding litharge, salt and water together whereby an oxychloride is formed.

$$4PbO + 2NaCl + 5H_2O = PbCl_2, 3PbO, 4H_2O + 2NaOH.$$

Carbon dioxide is then passed in:

$$3[PbCl_2, 3PbO, 4H_2O] + 6NaOH + 8CO_2 = 6NaCl + 11H_2O + 4[2PbCO_3, Pb(OH)_2].$$

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The white lead should be washed by decantation and dried carefully at 100°.

D. DOUBLE SALTS.

Roughly speaking, these fall into two classes.

I. **True double salts,** in which the acid hydrogen is replaced partly by one positive radical and partly by another, *e.g.*

$KNa(C_4H_4O_6)$, Rochelle salt.

$NaNH_4HPO_4$, microcosmic salt.

$MgNH_4PO_4$, magnesium ammonium phosphate.

On this view, monobasic acids cannot form true double salts. The sum of the valencies of the positive radicals is not greater than that of the acid radical.

II. **"Molecular" compounds.**—The sum of the positive valencies is greater than that of the acid radical.

These again fall roughly into two classes:

(*a*) In which the solution exhibits the usual qualitative reactions in a quantitative manner, *e.g.* the alums, substituted vitriols, etc.

(*b*) In which it does not, but in which either the kation or anion is a "complex," exhibiting none of the reactions of its constituents, *e.g.* the ferri-cyanides (no reaction for iron), the "metal ammines," etc.

No really sharp line can be drawn between (*a*) and (*b*) for all degrees of stability of the complex ion are exhibited; thus $K_3Fe(CN)_6$ gives no reactions for iron, whereas in $K_3Fe(C_2O_4)_3$ the iron is *partly* precipitated by caustic soda, showing that in solution the complex ion $Fe(C_2O_4)_3'''$ is partly dissociated.

$$Fe(C_2O_4)_3''' \rightleftharpoons Fe^{\cdot\cdot\cdot} + 3C_2O_4'',$$

though in accordance with the Mass Law, excess of $(C_2O_4)''$ ions (addition of a soluble oxalate) will suppress the iron reactions altogether. In the case of the alums, etc., the complex ion, if it exists, is completely broken down in solution, and thereby the salt exhibits quantitatively the reactions for its constituents.

Though a complete account of these interesting compounds cannot be given here, yet they have, in the hands of **A. Werner**, given rise to such important ideas as to the structure of inorganic substances, that an outline of the modern theory is given.

Briefly, most of these compounds fall into two classes, in which one ion is a complex consisting of the metal of higher valency, and usually six or four other monovalent (or an equivalent of polyvalent) radicals.

The general formula of this complex ion is $MA_{6 \text{ or } 4}$ or $MX_{6 \text{ or } 4}$ where M is the metal and A is NH_3 (or an amine) or H_2O, and X is an acid radical (usually Cl, etc., CN, NO_2, $\underset{2}{\underline{C_2O_4}}$, $\underset{2}{\underline{SO_4}}$, $\underset{2}{\underline{CO_3}}$.

The ion MA_6 exhibits the same valency as M, but A can be replaced, one at a time, by X, with a corresponding expected change in the valency. We thus get the following series of salts, in the case of the trivalent metals, which are ionised as indicated.

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$[MA_6]^{\cdot\cdot\cdot}X'_3$	*e.g.* $[Co(NH_3)_6]Cl_3$,	Hexammine cobaltichloride.
$[MA_5X]^{\cdot\cdot}X'_2$	*e.g.* $[Co(NH_3)_5Cl]Cl_2$,	Chloropentammine cobaltichloride.
$[MA_4X_2]^{\cdot}X'$	*e.g.* $[Co(NH_3)_4Cl_2]Cl$,	Chlorotetrammine cobaltichloride.
$[MA_3X_3]$ non-ionised, and showing no reactions for M, A or X.		
	e.g. $[Co(NH_3)_3(NO_2)_3]$	Trinitrito triammine cobalt.
$m^{\cdot}[MA_2X_4]'$,	*e.g.* $K[Co(NH_3)_2Cl_4]$,	Potassium diammine cobalt tetrachloride.
$m_2^{\cdot}[MAX_5]''$	*e.g.* $K_2[Ir(H_2O)Cl_5]$,	Potassium aquoiridium pentachloride.
$m_3^{\cdot}[MX_6]'''$	*e.g.* $K_3[Fe(CN)_6]$, $K_3[Co(NO_2)_6]$, etc.,	Potassium cobaltinitrite.

Similar series are known with the tetravalent metals, *e.g.* Pt, and are indicated, but as yet incomplete, with the divalent ones, *e.g.* Ni, etc. These and their ionisations may be worked out on the above lines by the student.

Series are also known in which the extreme complexes are MA_4 and MX_4. It should be clearly understood that the chemical and physical properties of the above substances are expressed completely by the above ionisations, *in freshly-made solutions.*

Werner assumes that the metals have the power of exerting some form of subsidiary valency and of "co-ordinating" 6 or 4 monovalent radicals (possibly other numbers also). It is clearly seen that the nature of the complex ion thus formed *is fully determined by the natures of the coordinated radicals and the metal.*

The extreme complex MX_6 is one of the commonplaces of chemistry, being typified by the ferricyanides, cobalticyanides and -nitrites; ferric, chromic and aluminic oxalates, etc.

It has been mentioned above that A in the complex may be water, as well as ammonia, amines, etc. We thus expect a series of complexes

$$[M(H_2O)_6], [M(H_2O)_5X] \ldots\ldots\ldots\ldots [MX_6].$$

Such series exist *in the hydrated salts, simple and double.* The subject cannot here be developed further, but must be left to the student, with the remark that the theory thus brings very many salts into line as one large class in which the metal exhibits the phenomenon of coordination.

It should be stated that these series are by no means complete and open up a wide field for research.

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EXAMPLES.

I. TRUE DOUBLE SALTS.

The general method of preparation is simply to mix solutions of the simple salts in the required proportions.

In some cases the acid salt of one base is neutralised by the other base.

70. **Rochelle (Seignette's) salt, $KNa(C_4H_4O_6),4H_2O$.**—Weigh out the required quantities of cream of tartar and sodium carbonate. Dissolve the latter in water, heat and add gradually the former in the solid form. Crystallise as far as possible, and recrystallise the mixed fractions to obtain large crystals.

$$2KH(C_4H_4O_6) + Na_2CO_3 = 2KNa(C_4H_4O_6) + CO_2 + H_2O.$$

71. **Potassium antimonyl tartrate (tartar emetic), $2K(SbO)C_4H_4O_6), H_2O$.**—To some cream of tartar add twenty times its weight of water and raise to the boil in a large basin. Add gradually pure antimony trioxide (from No. 18) till rather more than the theoretical amount has been added. Boil gently for half an hour, keeping up the volume of the solution. Filter whilst hot and set aside to crystallise. (Rhomic octahedra.)

$$2KH(C_4H_4O_6) + Sb_2O_3 = 2K(SbO)(C_4H_4O_6) + H_2O.$$

72. **Microcosmic salt, $NaNH_4HPO_4,4H_2O$.**—Mix solutions of Na_2HPO_4 and $(NH_4)_2HPO_4$ in molecular proportion. These may be obtained by neutralising equal volumes of ortho-phosphoric acid with soda and ammonia respectively, using litmus as indicator.

$$Na_2HPO_4 + (NH_4)_2HPO_4 = 2NaNH_4HPO_4.$$

73. **Magnesium ammonium phosphate, $MgNH_4PO_4,6H_2O$.**—(See Gibbs, *Amer. Jour. Sci.* [3], **5**, 114; Neubauer, *Zeit. angew. Chem.*, **1896**, p. 439.)

To a boiling solution of pure magnesium sulphate add slowly a solution of microcosmic salt (diluted mother-liquor from No. 72) till no more precipitate falls.

$$2MgSO_4 + 2NaNH_4HPO_4 = 2MgHPO_4 + Na_2SO_4 + (NH_4)_2SO_4.$$

Allow to cool and add some excess of ammonia.

$$2MgHPO_4 + 2NH_4OH = 2MgNH_4PO_4, 6H_2O.$$

Filter at the pump, wash with dilute ammonia, and dry between filter-paper. The corresponding arsenate may be made by using sodium arsenate (No. 95). Corresponding cobalt and manganese phosphates are known.

II. "MOLECULAR" COMPOUNDS.

(*a*) The best known of these are the "substituted vitriols," whose general formula is $M^{ii}SO_4, m^{i}_2SO_4, 6H_2O$,

where M^{ii} = Fe, Ni, Co. Mn, Zn, Mg, Cu, Cd,

and m^{i} = K, Na, NH_4, Rb, Cs, and sometimes Tl^{i}.

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A detailed account of the preparation of these important and beautiful salts is unnecessary; the general method is simply to mix solutions of molecular proportions of the two simple salts, and crystallise. These molecular proportions are obtained either by weighing out the pure substances, or by neutralising equal volumes of the diluted sulphuric acid by the two required bases or carbonates (or metals if possible).

The most important salt of the series is Mohr's salt,

$$FeSO_4, (NH_4)_2SO_4, 6H_2O,$$

(see Volumetric Analysis), which is obtained by the latter method, the solutions of each salt being so strong that when mixed hot the salt crystallises on cooling (see ferrous sulphate, No. 39).

Occasionally some difficulty is experienced in getting a well-crystallised specimen. This is the case especially with the manganese salts. The MnK salt has not yet been successfully prepared, and the $Mn(NH_4)$ salt should be allowed to crystallise spontaneously from a saturated solution.

Large crystals of these salts are readily grown by the usual methods. The $NiNH_4$ salt gives specially beautiful crystals. The crystals all belong to the monoclinic system.

Isomorphous selenates are well known also. See *Crystalline Structure and Chemical Composition.* Tutton. (Macmillan.)

The Alums.—These salts have the formula

$$R^{iii}(SO_4)_3, m^{i}_2SO_4, 24H_2O,$$

where R^{iii} = Fe, Cr, Al and sometimes Mn^{iii} (unstable);
m^{i} = K, NH_4, Rb, Cs. (Na alums not yet successfully prepared.)

74. **Potash Alum, $Al_2(SO_4)_3, K_2SO_4, 24H_2O$.**—Mix equimolecular proportions of the two salts, $Al_2(SO_4)_3,18H_2O$ and K_2SO_4, dissolved separately in water. $(NH_4)_2SO_4$, instead of K_2SO_4, gives ammonia alum. The former is the better to use for growing large well-shaped crystals. These form best at 13·5° C.

75. **Iron alum (potash or ammonia), $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$.**—To 500 c.cs. of water add 50 grams of strong sulphuric acid. Warm in a large basin, and add gradually 278 grams of crystalline ferrous sulphate. Boil gently, and add *cautiously* strong nitric acid, until a small portion gives, when treated with ammonia, pure ferric hydroxide (red-brown).

$$2FeSO_4 + H_2SO_4 + O(\text{from } HNO_3) = Fe_2(SO_4)_3 + H_2O.$$

The oxygen is supplied thus:

$$2HNO_3 = H_2O + 2NO + 3O.$$

(Rather more than the indicated amount of HNO_3 is required.)

As long as any ferrous sulphate is left, the NO formed dissolves in it to produce a dark brown solution.

Excess of nitric acid should now be driven off by evaporating on a *water-bath* to a thick syrup. This is diluted with 600 c.cs. of hot water, and a hot solution of 66 grams of ammonium sulphate (or the corresponding weight of potassium sulphate in as little hot water as possible) is mixed with it. The whole is set aside in a large crystallising dish.

Very beautiful crystals (amethyst-coloured) are readily grown.

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76. **Chrome-alum, $Cr_2(SO_4)_3,K_2SO_4,24H_2O$.**—The molecular proportions of chromic and alkali sulphate are best obtained by reducing a solution of potassium (or ammonium) dichromate, either by sulphur dioxide or alcohol.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O = \underset{\text{(aldehyde)}}{3C_2H_4O} + Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O,$$

or $$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

Dissolve 1 gm.-mol. of potassium dichromate (or the corresponding weight of ammonium dichromate) in 950 c.cs. of water in a porcelain basin (heating if necessary), and *carefully* add 4 gm.-mols. of sulphuric acid (pure acid of commerce is about 97% H_2SO_4). Cool by floating on ice cold water, and *carefully* add methylated spirits. Stir well, and do not allow the temperature to rise above 50-60° C. Reduction is complete when the smell of aldehyde (B.P. 21° C.) has disappeared. An excess of methylated spirits will do no harm, but will help to precipitate the alum. Leave overnight. A violet crystalline powder will be found, which is washed on the filter-pump with small quantities of ice-water till free from green colour.

It is now dissolved in as little water as possible at 40° C. (At higher temperatures a non-crystallisable variety will probably be formed.) Stand aside to crystallise. Perfect crystals are readily obtained.

The alums are isomorphous, and mixed saturated solutions of the various alums deposit mixed crystals, whose colour varies with the relative amounts of each kind present. Magnificent crystals may be obtained by mixing 1 part of a saturated chrome alum solution with 5 parts of a saturated potash alum solution.

Also a crystal of chrome alum, suspended in a saturated solution of another alum, will continue growing; beautiful crystals may thus be produced, having a chrome alum centre, surrounded by iron alum, and enclosed in potash alum. The last is the most difficult to grow successfully; the crystals deposit best at a temperature of 13·5° C.

(*b*) Salts containing a Complex Ion.

The commonest type of these contains the anion MX_6, tetra- or tri-valent according as M is di- or tri-valent.

77. **Potassium ferricyanide, $K_3[Fe(CN)_6]$.**—Prepared by the oxidation of the ferrocyanide by means of chlorine. The gas is passed into a cold solution of the ferrocyanide until a test portion no longer gives a blue precipitate or colour with ferric chloride. Crystallise till free from chloride. A blue precipitate forming during evaporation is merely filtered whilst the liquid is hot.

$$2K_4[Fe(CN)_6] + Cl_2 = 2KCl + 2K_3[Fe(CN)_6].$$

78. **Sodium cobalti-nitrite, $Na_3[Co(NO_2)_6]$** (De Koningh's reagent).—To a solution of 50 gms. of cobalt nitrate and 150 gms. of sodium nitrite in 150 c.cs. of water at 40°-50° C., add slowly, with constant shaking, 25 c.cs. of glacial acetic acid. Filter off any precipitate which may form on standing, and remove oxides of nitrogen from the filtrate by a vigorous air-current, aspirated by means of a filter-pump.

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The substance is now precipitated by 400 c.cs. of alcohol (methylated spirits distilled from lime) allowed to stand for some time, filtered at the pump and washed with a little alcohol. The crude product is recrystallised (if required) from water.

The mother liquor may be converted into the potassium salt by the addition of a concentrated solution of potassium nitrate until no further precipitate falls. Stand overnight, filter, wash and dry in desiccator.

The reactions are as follows:

(1) Cobaltous nitrite is formed

$$Co(NO_3)_2 + 2NaNO_2 = 2NaNO_3 + Co(NO_2)_2.$$

(2) This is oxidised to cobaltic nitrite by free nitrous acid formed by sodium nitrite and acetic acid.

$$2Co(NO_2)_2 + 4HNO_2 = 2Co(NO_2)_3 + 2H_2O + 2NO.$$

(3) $$2Co(NO_2)_3 + 6NaNO_2 = 2Na_3[Co(NO_2)_6].$$

Used as a test for potassium and ammonium. See also separation of nickel and cobalt, p. 111.

78A. **Potassium cobalticyanide, $K_3[Co(CN)_6]$** (formed in the cyanide separation of nickel and cobalt, *q.v.*, p. 109) *J. prakt. Chem.* (2) **31**, 172.—Dissolve 30 gms. of cobalt carbonate in a slight excess of 50% acetic acid, and evaporate dry on a water-bath. Dissolve the residue in water, filter and add a filtered solution of 120 gms. of potassium cyanide. Now draw a rapid stream of air through the solution till the cobaltocyanide is completely oxidised, neutralise with acetic acid and evaporate the filtered solution to crystallisation. Filter off the crystals and wash with 70% alcohol.

$$Co(C_2H_3O_2)_2 + 2KCN = Co(CN)_2 + 2K(C_2H_3O_2)$$
$$Co(CN)_2 + 4KCN = K_4[Co(CN)_6]$$
$$2K_4[Co(CN)_6] + O + H_2O = 2K_3[Co(CN)_6] + 2KOH.$$

79. **Potassium chromoxalate, $K_3[Cr(C_2O_4)_3]$.**—Potassium dichromate acts on oxalic acid thus:

$$K_2Cr_2O_7 + 7H_2C_2O_4 = 7H_2O + 6CO_2 + K_2C_2O_4 + Cr_2(C_2O_4)_3.$$

The two oxalates then form the complex salt, more potassium oxalate being required for the complete conversion

$$3K_2C_2O_4 + Cr_2(C_2O_4)_3 = 2K_3[Cr(C_2O_4)_3].$$

No chromium ions are present, the salt being ionised as indicated,

$$K_3[Cr(C_2O_4)_3] \rightleftarrows 3K^{\cdot} + [Cr(C_2O_4)_3]'''.$$

The extra potassium oxalate may be added in the form of KHC_2O_4, the reaction then becoming

$$K_2Cr_2O_7 + 4KHC_2O_4 + 5H_2C_2O_4 = 7H_2O + 6CO_2 + 2K_3[Cr(C_2O_4)_3],$$

or as the "quadroxalate,"

$$K_2Cr_2O_7 + 4KHC_2O_4, H_2C_2O_4 + H_2C_2O_4 = 7H_2O + 6CO_2 + 2K_3[Cr(C_2O_4)_3].$$

Weigh out quantities of each substance in the required proportions (oxalic acid $= H_2C_2O_4, 2H_2O$, the quadroxalate also having two molecules of water

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of crystallisation). Dissolve the oxalate and acid in a minimum of hot water, and the dichromate in another portion. Filter and add the oxalate slowly to the dichromate, allow to simmer till evolution of carbon dioxide ceases, and set aside to cool. Drain the crystals, work up the mother liquor for a further yield, and recrystallise the whole.

80. **Potassium ferric-oxalate, $K_3[Fe(C_2O_4)_3]$** may be prepared by mixing solutions of the required quantities of ferric chloride and potassium oxalate,

$$2FeCl_3 + 6K_2C_2O_4 = 6KCl + 2K_3[Fe(C_2O_4],$$

which forms magnificent green crystals.

The complex ion $[Fe(C_2O_4)_3]'''$ is less stable than the chromoxalion, and the solution therefore gives the reactions for the ferric ion, though not quantitatively.

$$[Fe(C_2O_4)_3]''' \rightleftarrows Fe^{\cdot\cdot\cdot} + 3(C_2O_4)''.$$

By increasing the concentration of the oxalion (adding a soluble oxalate) the ferric ion can be suppressed in accordance with the Mass Law.

Potassium aluminium oxalate is similarly prepared, the complex ion being still less stable.

The preparation of the other types of complex salts is given below. The general scheme is as follows:

Cobaltous salts, treated with excess of ammonia solution form hexammine cobalt*o* salts. When these are oxidised by an air-stream in the presence of ammonium carbonate, they form carbonato-tetrammine-cobalt*i* salts.

The "carbonato" portion of the complex is exchanged for other radicals by treatment with suitable reagents, thus with hydrochloric acid they form chloro-aquo-tetrammine salts, which by warming with ammonia form the aquo-pentammine salts. These again with hydrochloric acid form chloro-pentammine compounds, which by treatment with ammonia under pressure form the hexammine salts.

Scheme.

$$[Co(NH_3)_6]Cl_2 \xrightarrow[+\text{oxygen}]{(NH_4)_2CO_3} [Co(NH_3)_4CO_3]Cl \xrightarrow{+HCl} [Co(NH_3)_4(H_2O)Cl]Cl_2$$

$$[Co(NH_3)_4(H_2O)Cl]Cl_2 \xrightarrow{+NH_3} [Co(NH_3)_5(H_2O)]Cl_3 \xrightarrow{+HCl} [Co(NH_3)_5Cl]Cl_2$$

$$[Co(NH_3)_5Cl]Cl_2 \xrightarrow[\text{under pressure}]{+NH_3} [Co(NH_3)_6]Cl_3$$

81. **Type $[CoA_6]X_3$; $[Co(NH_3)_6]Cl_3$.** Jörgensen, *Zeit. an. Ch.*, **17**, 455.—5 parts of chloro-pentammine cobalt chloride (No. 82), 4 parts of ammonium chloride and 50 parts of 20% ammonia solution are mixed in a pressure flask, which is wrapped in a cloth and tied to a stick, so that it can be shaken without danger. It is immersed in cold water and slowly raised to a boil. The boiling is continued for 6 hours with occasional vigorous shaking. Considerable pressure is developed, and precautions against damage by the bursting of the flask should be taken. When the chloro-pentammine salt has almost disappeared the flask is allowed to cool, carefully opened and the contents

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poured into a large basin and left overnight for the ammonia to evaporate. The liquor is then diluted with 3 times its volume of water and ½ its volume of strong hydrochloric acid, and heated for an hour in a flask on a water-bath. Now add much strong hydrochloric acid, cool quickly under the tap with vigorous shaking and filter off the yellow product at the pump, washing with fairly strong hydrochloric acid. Recrystallise by dissolving in a little cold water, filter from unchanged pentammine salt, add ½ its volume of strong hydrochloric acid, and set aside. All the chlorine is precipitated by silver nitrate.

82. **Type** $[\mathbf{CoA_5X}]\mathbf{X_3}$; $[\mathbf{Co(NH_3)_5Cl}]\mathbf{Cl_2}$.—10 gms. of carbonato-tetrammine cobalt nitrate (No. 83) dissolved in 130 c.cs. of water are acidified with strong hydrochloric acid (till no more carbon dioxide is formed) and then rendered just alkaline with ammonia. 15 c.cs. of ·880 ammonia are then added and the whole heated for 3 hours on a water-bath. Cool and add 150 c.cs. of strong hydrochloric acid, heat up again, cool, filter and wash the product with alcohol. Yield about 8 gms. Two-thirds only of the chlorine are precipitated by silver nitrate.

83. **Type** $[\mathbf{CoA_4X_2}]\mathbf{X}$; $[\mathbf{Co(NH_3)_4CO_3}]\mathbf{NO_3}$. Jörgensen, *Zeit. an. Ch.*, **2**, 282.—Dissolve 50 gms. of crystalline cobalt nitrate in 80 c.cs. of water, pour it, with stirring, into 250 c.cs. of ·880 ammonia, 100 gms. of ammonium carbonate and 500 c.cs. of water. Place in a large flask and draw a rapid air-stream through it, by means of the filter-pump, for 3 hours. Then evaporate halfway, adding at regular intervals small portions of ammonium carbonate (30 gms. altogether), filter immediately and boil down to 200 c.cs. with further addition of 10 gms. of ammonium carbonate in portions. Cool, filter and wash with water and alcohol. Yield, 50-60 gms.

84. **Type** $[\mathbf{CoA_3X_3}]$. $[\mathbf{Co(NH_3)_3(NO_2)_3}]$. Jörgensen, *Zeit. an. Ch.*, **17**, 475.—45 gms. of cobalt chloride crystals are dissolved in 125 c.cs. of water and mixed with a cold solution of 50 gms. of ammonium chloride and 67 gms. of sodium nitrite in 375 c.cs. of 20% ammonia. Pass a rapid air-stream, by means of the filter-pump, for 4 hours, set in open basins for 2 days for the ammonia to evaporate, filter and wash with cold water till free from chloride.

The freshly-made solution is practically a non-conductor, and does not show the reactions either for cobalt or a nitrite.

85. **Type** $\mathbf{m}[\mathbf{Co(A)_2X_4}]$. $\mathbf{K}[\mathbf{Co(NH_3)_2(NO_2)_4}]$. Jörgensen, *J. pr. Ch.*, (2), **23**, 249.—Treat 10 gms. of cobalt carbonate with hydrochloric acid just insufficient for complete solution. Dilute to 200 c.cs., add 70 gms. of ammonium chloride and having warmed the whole add it slowly to a warm solution of 100 gms. of potassium nitrite in 100 c.cs. of water. Warm to about 80° for half an hour, then keep at 0° for 24 hours. A yellow powder and compact brown crystals separate; the former is readily separated by stirring up well and decanting from the crystals. The latter are dried with filter-paper. The substance is known as Erdmann's salt.

Type $\mathbf{m_2}[\mathbf{MAX_5}]$. This type was unknown until recently, when Delépine prepared $K_2[Ir(H_2O)Cl_5]$. This, however, is not a useful preparation for the student. See *Compt. Rend.*, 1908, **146**, 1267.

Several substances representing the type $m_3[MX_6]$ have been described above.

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A few more interesting and important salts, belonging to other series of complexes, are described below.

86. **Cuprous mercuryiodide, $Cu_2[HgI_4]$.** *Ber.* **3** (1870), 123.—13·6 gms. of mercury chloride dissolved in water are added to a solution of 16·6 gms. of potassium iodide. The precipitated mercury iodide is washed by decantation and dissolved in 16·6 gms. of potassium iodide in 100 c.cs. of water. The clear solution is added to a solution of 24 gms. of copper sulphate crystals in 70 c.cs. of water, and a fine red crystalline precipitate slowly forms.

Reduction to the cuprous salt is completed by passing in sulphur dioxide. Filter at the pump, wash with water and dry at 100°. The salt is remarkably sensitive to heat, a sharp colour change taking place at 71° C. A corresponding silver salt, prepared as above (no reduction being necessary), is also sensitive to heat. The potassium salt is formed by the solution of the mercuric iodide in the iodide solution, and crystals may be obtained by evaporation *in vacuo*.

87. **Cadmium iodide, $Cd[CdI_4]$.** Hittorf, *Pogg. Ann.*, **106**, 545.—This remarkable substance is an "auto-complex," being ionised as indicated, and is thus the cadmium salt of H_2CdI_4.

Spongy cadmium, obtained by adding zinc to a solution of cadmium sulphate, is suspended in water, some excess of iodine added, and the whole boiled in a flask fitted with a reflux condenser till the metal has dissolved. Remove the condenser and boil off the excess of iodine, filter and crystallise. Obtain a further crop from the liquor.

88. **Aquo-tetrammine-copper sulphate, $CuSO_4, 4NH_3, H_2O$.**—This substance is formed when ammonia in excess is added to copper sulphate solution. To 200 c.cs. of a 30% solution of copper sulphate add ammonium hydroxide until the blue precipitate is completely dissolved. Place in a beaker, and carefully run on to the surface a layer of water 1 cm. deep. On this run a layer of alcohol several cms. deep. (These layers should be carefully put on from a dropping funnel.) As the liquids diffuse into one another through the water, fine crystals of the substance gradually grow on the sides of the beaker. After about a week they may be removed, dried quickly with filter-paper and preserved in a stoppered bottle.

A corresponding zinc compound is known, which is similarly made.

89. **Pentammine copper sulphate, $CuSO_4, 5NH_3$.** May be regarded as copper sulphate in which the water of crystallisation has been replaced by ammonia. It is formed when dry ammonia gas is led over anhydrous copper sulphate. A fine violet powder is produced which is fairly stable.

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CHAPTER VI.

ACIDS AND ACID ANHYDRIDES.

A. ACIDS.

THE general method for the preparation of an acid is to act on a salt of the required acid by means of a "stronger" acid, *e.g.*

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3(PO_4)_2.$$

Many of the oxyacids (non-metallic hydroxides) may be prepared by the direct oxidation of the non-metal by means of strong nitric acid, *e.g*

$$2P + 6HNO_3 = 2HPO_3 + 2H_2O + 2NO + 4NO_2.$$

The particular oxides of nitrogen and the amounts of each produced, will be determined by the strength of the nitric acid; if only the strongest acid will react, more NO_2 will be produced, and so on.

90. **Nitric acid, HNO_3, from Chili saltpetre.**—170 gms. of sodium nitrate and 200 gms. of strong sulphuric acid are placed in a large retort and heated gently on a wire gauze. The nitric acid distils and is received in a flask which is kept cool by a stream of water from the tap. The acid thus obtained will contain about 20 % of water (average), and some sulphuric acid carried over mechanically. Hydrochloric acid will also generally be present unless the nitrate used is free from chloride (*e.g.* pure KNO_3).

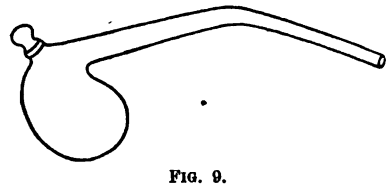

FIG. 9.

Pure nitric acid (almost anhydrous) may be obtained as follows:

The above distillate is placed in a retort of which the neck has been drawn out somewhat and bent to an angle of about 120°. This is inclined so that sulphuric acid carried over mechanically runs back into the retort. A condenser is attached, an equal volume of pure sulphuric acid is added to the nitric, and it is *slowly* distilled. If the original acid contains hydrochloric, the receiver is changed when the distillate, diluted with water, no longer reacts with silver nitrate.

The acid still contains oxides of nitrogen which may be removed by a rapid stream of dry air filtered from dust.

The liquid must be kept in the dark. Nitric acid boils at about 86° C. and has a specific gravity of about 1·54. If coloured yellow, it contains oxides of nitrogen in solution.

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Test for sulphuric acid by diluting several c.cs. with water and adding barium chloride.

91. **Phosphoric acid (glacial), HPO_3, from bone-ash.**—To a litre of 5N sulphuric acid, heated in a large basin to about 80° C., add gradually rather less than the calculated quantity of calcium phosphate (bone-ash). Stir thoroughly and boil well for half an hour, adding water to keep up the original volume. Allow to cool, and filter on the pump, using a large funnel. Wash the residue with a little very dilute sulphuric acid and alcohol. Evaporate the filtrate and washings (using a smaller basin as the volume diminishes), until sulphuric acid fumes begin to come off. Then heat on a wire gauze in a fume-cupboard until these fumes cease. The residue when cool sets to a glassy mass of meta-phosphoric acid, which is sealed up in a bottle.

N.B.—During the evaporation, a small precipitate of calcium sulphate may form.. This should be filtered off.

92. **Phosphoric acid from phosphorus.**—25 grams of red phosphorus are placed in a large basin in a fume-cupboard, and covered with moderately strong nitric acid (1 : 1). Heat gently on a sand-bath till the reaction starts, then remove the bunsen. The reaction is very vigorous at first, but subsides quickly. More strong nitric acid is gradually added, allowing the reaction to subside each time, until the oxidation proceeds quietly. Now boil with nitric acid until the oxidation is complete, evaporate off most of the nitric acid, dilute with water, filter, and again evaporate till fumes cease to be evolved.

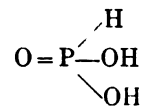
Some authorities advocate yellow phosphorus. This reaction requires the greatest care, as it is apt to be explosively violent. The nitric acid must have a specific gravity of *not more than* 1·2, but should be very little less, or the reaction is very prolonged. Ortho-phosphoric acid may be prepared from the glacial acid by prolonged boiling (at least an hour) with considerable water, and subsequent evaporation to a temperature of about 185°. Then evaporate *in vacuo*, when it will form colourless crystals.

93. **Phosphorous acid, H_3PO_3.**—Reaction :

$$H_2C_2O_4 . 2H_2O + PCl_3 = H_3PO_3 + 3HCl + CO + CO_2.$$

Place the calculated quantities of the reagents in a flask fitted with a reflux condenser. Heat very cautiously till the reaction has entirely ceased. Allow to cool in a basin in a desiccator.

Note that phosphorous acid is only dibasic ; its constitution is therefore most probably



(*Cf.* hypophosphorous acid.)

94. **Hypophosphorous acid, H_3PO_2.** Dulong, *Ann. Chim. Phys.*, 1816, p. 141.—Fit a round-bottomed 2 litre flask as shown in Fig. 10. In it place a solution of 120 gms. of barium hydroxide in 1200 c.cs. of water, and add 30 gms. of yellow phosphorus. The apparatus is fixed in a fume-cupboard, the air displaced by a rapid stream of coal gas and the delivery tube then

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placed under water. The flask is carefully heated (sand-bath) until the phosphorus has gone completely into solution, phosphine (spontaneously inflammable) being evolved, each bubble inflaming on contact with the air, producing a fine vortex ring of phosphoric acid. Now pass into the *hot* liquor a stream of carbon dioxide to precipitate excess of baryta, filter and concentrate till crystallisation begins (filtering off any barium carbonate that may precipitate during the evaporation), add some alcohol and set aside to crystallise. Filter at the pump, and obtain another crop from the filtrate. Re-crystallise the mixed products from as little hot water as possible. Fine crystals of barium hypophosphite are readily obtained, $Ba(H_2PO_2)_2 . H_2O$.

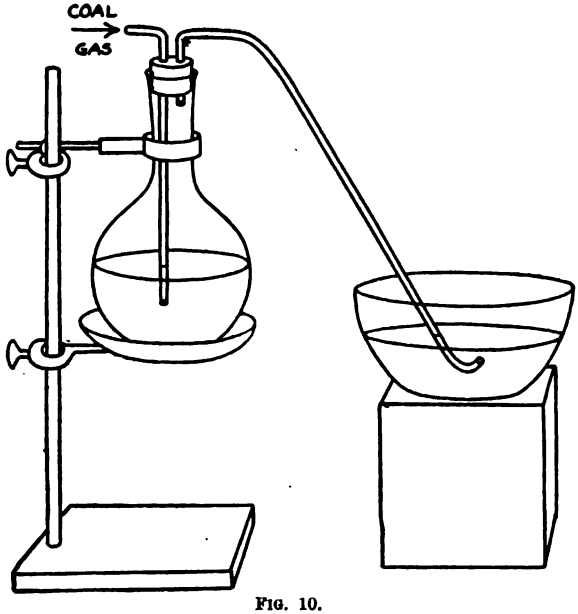


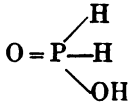
FIG. 10.

The free acid is made by weighing out a quantity of the crystals, dissolving in water and adding the *exact* amount of 8N sulphuric acid. Filter and evaporate *slowly* till temperature reaches 130° C. Filter if necessary and cool on ice. Do not attempt this preparation with small quantities.

Reactions: $3Ba(OH)_2 + 8P + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2$,

$3Ba(H_2PO_2)_2 + 3H_2SO_4 = 3BaSO_4 + 6H_3PO_2$.

The acid is *mono-basic only*, and has therefore the structure



It is decomposed by heat thus: $4H_3PO_2 = H_4P_2O_7 + H_2O + 2PH_3$.

It is a very powerful reducing agent (try silver nitrate, mercuric chloride, etc.), and reduces copper sulphate to copper hydride, Cu_2H_2. This is obtained

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by adding considerable dilute hypophosphorous acid to a 25 % solution of copper sulphate at 30° C. (See Wurtz, *Ann. Chim. Phys.*, 1844, p. 250.)

95. **Arsenic acid, $2H_3AsO_4 + H_2O$.**—Prepared from the residue in the preparation of nitrous anhydride. Decant the liquor from any unchanged arsenious acid, and evaporate to dryness. Re-dissolve in a little water, evaporate to a syrup, cover up and allow to crystallise in a cold place. It is a little difficult to hit off the correct concentration for obtaining large crystals, and if necessary, trials must be made. The crystallisation is very slow in starting, and it may be necessary to add a crystal (obtained by evaporating a drop to dryness) to give it a start.

96. **Boric acid (H_3BO_3, ortho-boric) from borax.**—Borax, $Na_2B_4O_7,10H_2O$ (*i.e.* pyro-borate) is dissolved in boiling water and a very slight excess of strong hydrochloric acid added. The borax solution should be about 20 %, when the acid crystallises on cooling. Filter at the pump, wash with ice water, and dry at 120°.

$$Na_2B_4O_7 + 2HCl + 5H_2O = 4H_3BO_3 + 2NaCl.$$

97. **Iodic acid, HIO_3, $2H_2O$.**—Two methods:

(1). Decompose barium iodate by the *exact* amount of dilute sulphuric acid. Filter and evaporate to crystallisation.

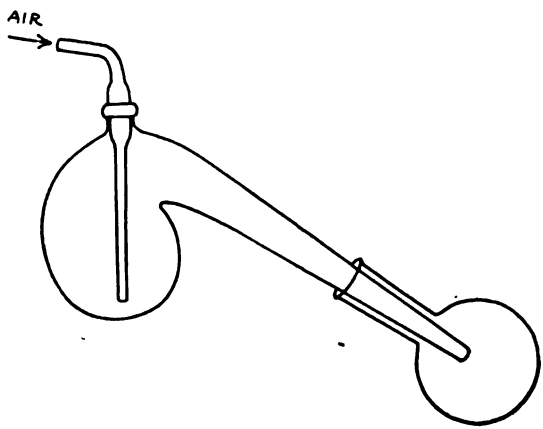

FIG. 11.

(2) Oxidise iodine by strong nitric acid.

Thirty grams of iodine and 130 grams of nitric acid (free from nitrous) are put in a retort fitted as shown. Gentle heat is applied and the oxides of nitrogen produced are removed by blowing air through the tube, as these reduce the iodic acid and hence retard the oxidation. Any iodine that distils is put back into the retort from time to time. When completely oxidised, evaporate off the nitric acid and crystallise from water.

At 200° C. the anhydride I_2O_5 is formed, which decomposes at higher temperatures. Prepare this from the mother-liquor.

B. ACID ANHYDRIDES.

98. **Iodic anhydride, I_2O_5.**—(See No. 97).

99. **Chromic anhydride, CrO_3** (H_2CrO_4 known only in solution).

Reaction: $$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + H_2O + 2CrO_3.$$

100 grams of potassium dichromate are dissolved in 170 c.cs. of boiling water in a large porcelain basin. To this add *very slowly and cautiously* 125

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c.cs. of strong sulphuric acid. Stand overnight. Decant from the bisulphate and drain the crystals as far as possible. Heat the liquor to 85° C. and add some more sulphuric acid (100 c.cs. of the *bench* acid). Evaporate on the water-bath till the surface is covered with a crystalline mass of the anhydride, and set aside overnight. Filter through asbestos on the pump, and work up the mother-liquor. The anhydride is still contaminated with sulphuric acid, which is removed by washing it on the pump with concentrated nitric acid. Finally heat in an open basin to a temperature not exceeding 150° C. to get rid of nitric acid. (M.P. = 192° C.)

The large excess of sulphuric acid employed is partly for Mass Law reasons, partly to assist in the crystallisation of the $KHSO_4$.

100. **Sulphuric anhydride, SO_3.**—Reaction :

$$2SO_2 + O_2 \rightleftarrows 2SO_3 \text{ (in presence of catalyst).}$$

Sulphur dioxide and oxygen in volume ratio 2 : 1 (approx.) are passed over freshly-prepared platinised asbestos at a temperature of 400° C. The

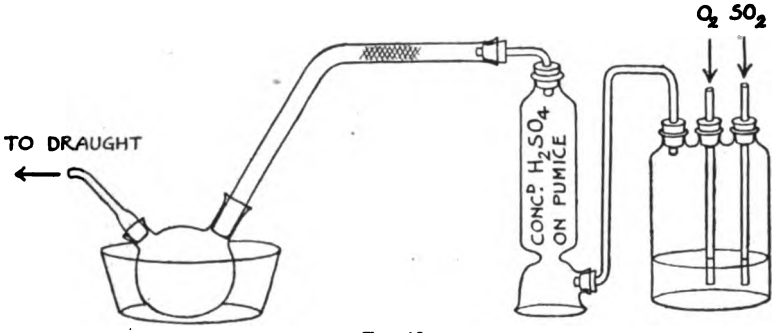

FIG. 12.

SO_3 is condensed in a freezing mixture, at a temperature not lower than −5° C. The essential necessary to success is the absolute exclusion of moisture from the whole apparatus. No corks should be used which are likely to come into contact with the anhydride. The temperature of the freezing mixture must not be too low, or any excess of SO_2 will be liquefied (−10° C.). The sulphur dioxide may be delivered from a syphon and the oxygen from a gas-holder or a cylinder fitted with a regulator. The apparatus explains itself.

The platinised asbestos is prepared by soaking asbestos wool in a solution of chlorplatinic acid and igniting it strongly. As soon as a sufficient quantity of the trioxide has formed in the receiver, the delivery tube is removed and the neck sealed off by the help of a Herapath mouth blow-pipe, without removing the flask from the freezing misture.

101. **Nitrous anhydride, N_2O_3.** ($NO + NO_2$).—First shown to exist in the *gaseous* state by Dixon and Peterkin, *J.C.S.*, 1899, p. 613. Baker showed that when quite dry (in presence of nitrogen), not only was it not dissociated, but might even be N_4O_6 (see *J.C.S.*, 1907, p. 1862).

Reaction : $$As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3.$$

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50 grams of arsenious oxide (small lumps) are placed in a small long-necked flask fitted with a thistle-funnel and a right-angled outlet tube. This is connected to a small drying tube containing phosphoric anhydride, which in turn is connected to a U-tube surrounded by a freezing mixture. 50 c.cs. of strong nitric acid are poured through the thistle tube, and the flask, standing on an asbestos pad, is warmed gently. The anhydride is a deep-blue liquid. When the reaction is over the U-tube is sealed whilst still in the freezing-mixture.

N_2O_3 forms nitrous acid with *ice-cold* water (blue solution), but some of it is always lost as NO, the NO_2 thus formed dissolving to form nitrous and nitric acids.

$$N_2O_3 + H_2O = 2HNO_2$$
$$N_2O_3 \rightleftarrows NO + NO_2$$
$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

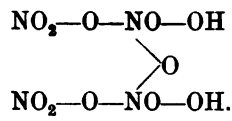
Utilise the residue in the flask for the preparation of arsenic acid, No. 95.

102. **Nitric anhydride, N_2O_5.**—(Deville, *Ann. Chim. Phys.* [3], **28**, 241 Weber, *Jour. Prakt. Chem.* [2], **6**, 342.)

Reaction: $$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3.$$

Two molecular proportions of pure anhydrous nitric acid are put into a beaker immersed in a freezing mixture, and *slightly* more than one molecular proportion of phosphoric anhydride added very gradually, taking care that the temperature does not at any time rise above 0° C. (Stir well with thermometer.) The product is transferred to a *large* dry retort (to allow for frothing) connected to a well-fitting receiver immersed in ice. Heat the retort cautiously on a water-bath; if care has been taken to exclude moisture, the distillate will solidify.

It is well not to preserve the product, but to use it up in investigating its properties. F.P. 5° C., M.P. 30° C. Decomposes rapidly above 45° C. (explosively when incautiously heated). Combines violently with water, and with strong nitric acid forms N_2O_5, $2HNO_3$, *i.e.*



103. **Phosphorous anhydride, P_4O_6.** (Thorpe and Tutton, *J.C.S.*, *1908*, 549; *1891*, 1019.)—Obtained when phosphorus is burnt in a limited supply of air in the apparatus shown. Even then the pentoxide is the principal product; separation is effected by taking advantage of the ready volatility of the lower oxide. The apparatus explains itself. The water in the condenser is kept at 50°-60°. The plug of glass-wool serves to keep back much of the pentoxide. The trioxide distils over into the small flask in the freezing mixture.

104. **Phosphoric anhydride, P_4O_{10}.**—Yellow phosphorus is burnt in a carefully regulated supply of dry air or oxygen. Apparatus for this purpose will be found in most catalogues. See also Roscoe and Schorlemmer, Vol. I.

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If the apparatus is not available, one may be improvised on the lines shown in Fig. 14.

The bell-jar stands on a glass plate, and the phosphorus on an iron tray (a clean sand-bath tray). The combustion is started in air, and oxygen admitted from a gas-holder or a cylinder fitted with a regulator, the supply

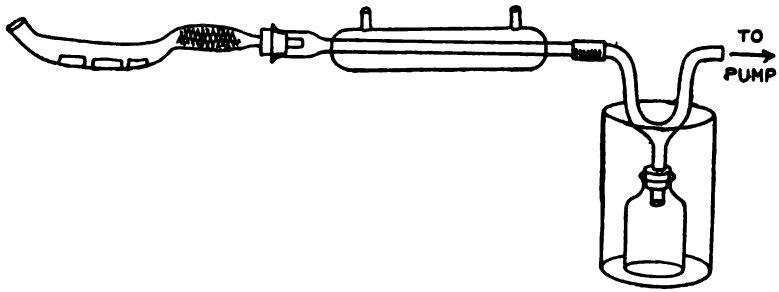

FIG. 13.

being controlled by a tap. The combustion should be fairly rapid, but should not be allowed out of control. Bottle up the product at once.

Vapour density experiments show that the formula is P_4O_{10}, not P_2O_5 as it was formerly written.

105. **Arsenious anhydride, As_4O_6.**—Occurs in three forms:

(1) Crystalline (octahedral and rhombic).

(2) Amorphous (vitreous) which is unstable and passes into the crystalline variety.

(1) **Crystalline As_4O_6.**—The starting-point is commercial arsenious oxide.

Method (*a*). Dissolve some of the oxide in 50 % potash solution and dilute twenty times with water. After some days, individual octahedra will form. Any crusts forming should be removed.

Method (*b*). The arsenic acid liquor from No. 95 is evaporated to dryness and dissolved in water to a syrup. This is diluted with twelve times its volume of a freshly-made saturated sulphur dioxide solution and stoppered up in a flask. After several weeks octahedra form. Filter, wash quickly with a little water, then with alcohol and ether.

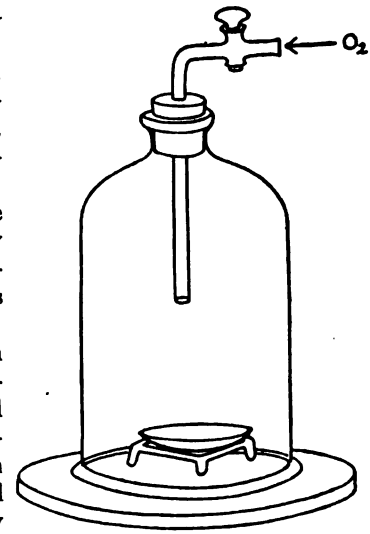

FIG. 14.

(2) **Amorphous As_4O_6** is prepared on the large scale by subliming the impure oxide from iron pots into cylinders placed over them.

106. **Arsenic anhydride, As_2O_5.**—The arsenic acid solution obtained in No. 95 is carefully dried and heated to 275° C. At higher temperatures it is decomposed,

$$As_2O_5 = As_2O_3 + O_2.$$

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On this account its vapour density cannot be found, and the simpler formula is therefore employed.

107. **Silicic anhydride, SiO_2.**—*Reactions*:

$$4HF + SiO_2 \text{ (in any silicate)} = 2H_2O + \underset{\text{gas.}}{SiF_4}.$$

On passing into water $$3SiF_4 + 4H_2O = 2H_2SiF_6 + \underset{\text{ppt.}}{H_4SiO_4}.$$

and on ignition $$H_4SiO_4 = SiO_2 + 2H_2O.$$

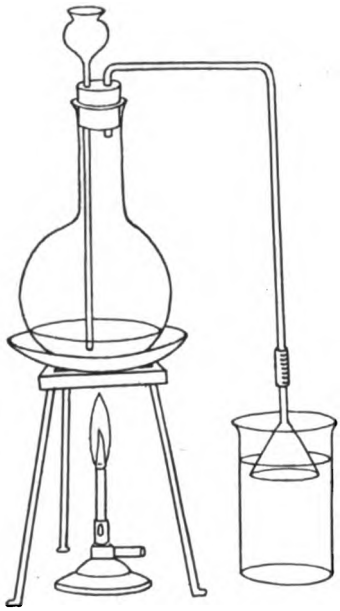

FIG. 15.

An intimate mixture of 3 parts of calcium fluoride and 2 parts of common sand is introduced into a flask containing strong sulphuric acid. See that the mixture is thoroughly wetted by the acid, and then fit up as shown and heat gently. When the reaction is over, filter off the precipitated silicic acid, wash it, dry and ignite strongly. The product is a pure white amorphous powder. Convert the filtrate into potassium fluosilicate by adding a solution of potassium chloride.

$$2KCl + H_2SiF_6 = K_2SiF_6 + 2HCl.$$

Filter and wash the precipitate and dry in a desiccator.

Note.—If fluosilicic acid be treated with alkali, it is decomposed.

$$H_2SiF_6 + 6KOH = 6KF + H_4SiO_4 + 2H_2O.$$

Silica may be otherwise prepared from "water-glass" by strongly acidifying it with hydrochloric acid, evaporating dry, heating on a sand-bath to render the acid insoluble, and washing well with boiling water to free it from salt. Filter, wash, dry and ignite strongly.

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CHAPTER VII.

HALOGEN COMPOUNDS.

UNDER this heading are included :

I. Halogen acids and oxyacids not already given.

II. Metallic salts of the above.

III. Non-metallic chlorides and oxychlorides, especially "acid chlorides."

It often happens that these acids and salts are not conveniently prepared by the general methods for one of several reasons.

(*a*) The acids are not stable, *e.g.*

$$KI + H_2SO_4 \text{ does } \textit{not} \rightarrow KHSO_4 + HI,$$

for H_2SO_4 oxidises 2HI readily $\rightarrow H_2O + I_2$, and reduction products of the H_2SO_4, especially SO_2 and H_2S.

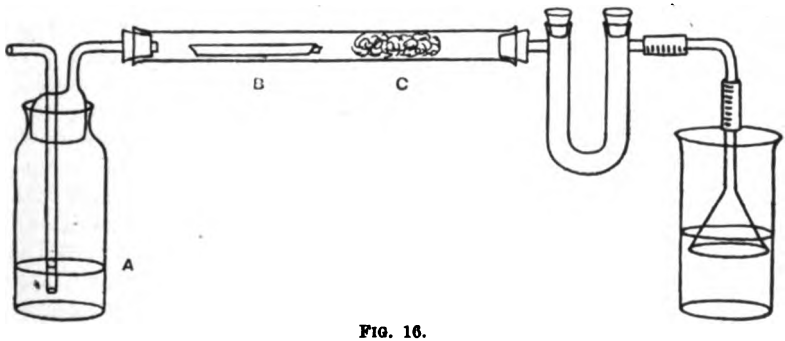

FIG. 16.

(*b*) The anhydrous metallic salts cannot be made from solution, as partial hydrolysis takes place. This is especially the case with the trivalent metals.

(*c*) The acid is not so readily available as the halogen itself ; *e.g.* hydriodic and chloric acids.

It will readily be seen which of these reasons applies in each of the following cases.

I. HALOGEN ACIDS AND OXY-ACIDS.

108. **Hydriodic acid, HI.**—This is best obtained by the direct combination of hydrogen and iodine under the influence of heated platinised asbestos. Fig. 16 shows the apparatus : hydrogen free from arsenic (from a Kipp) is dried in *A* by strong sulphuric acid. Iodine is placed in the boat *B* ; *C* is a plug of platinised asbestos (see p. 43). Disconnect the hydrogen apparatus

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and drying tower from the tube, and sweep all air out of the former by a stream of hydrogen before connecting, otherwise the mixture of hydrogen and air will be ignited by the catalytic action of even the cold platinised asbestos, and an explosion will result. Then connect to the tube, heat the platinum and slowly vaporise the iodine. The combination is practically complete with excess of hydrogen, but a U-tube containing a little moist red phosphorus may be used if desired. The hydrogen iodide is absorbed in water as shown in Fig. 17 or 18. Preserve in the dark.

Hydrobromic acid may be similarly prepared, with an obvious modification to contain the bromine. It may otherwise be made thus:

109. **Hydrobromic acid, HBr.**—*Reaction*:

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr.$$

30 grams of sand are placed in the flask (500 c.cs.) and on this a mixture of 31 grams of red phosphorus, 100 grams of sand and 60 c.cs. of water. 240

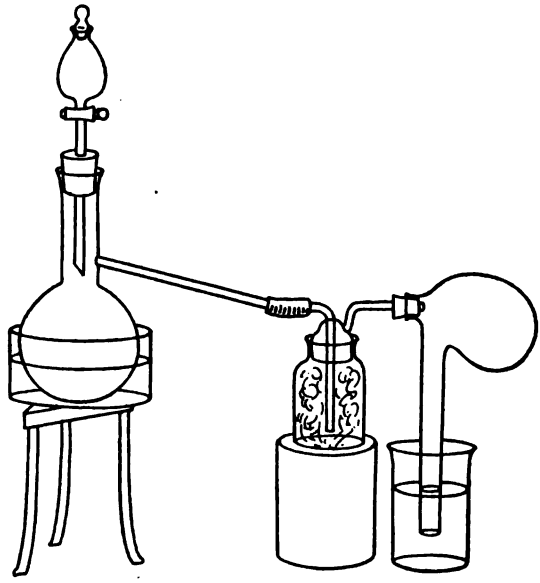

FIG. 17.

grams (80 c.cs.) of bromine are placed in the funnel. The wash-bottle contains a little glass-wool wetted with a cream of red phosphorus and water, to prevent free bromine being carried over. The retort delivery tube prevents "sucking back." Two wash-bottles arranged as shown in Fig. 18 may be used instead if desired. 100 c.cs. of water are placed in the absorber, and the bromine is carefully added, a little at a time. At the end of the reaction the flask may be placed in boiling water as shown. The function of the sand is to moderate the action, which might otherwise crack the flask. Preserve in the dark.

Hydriodic acid may be prepared analogously, but since iodine is a solid it cannot be added through a funnel; the water is thus added to the iodide previously prepared.

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110. **Hydrofluoric acid, HF.**—Powdered calcium fluoride is heated gently with strong sulphuric acid in a lead retort. The evolved gas is conducted by a leaden tube into water in a wax or gutta-percha bottle. This is really an example of the general method of preparing an acid, the apparatus only being of a special kind, owing to the action of the acid on glass or any silicate.

111. **Hypochlorous acid, HClO.**—This can be obtained in dilute solution in several ways; all attempts to concentrate the solution lead to its decomposition. The best way, however, is to pass chlorine over gently heated, precipitated mercuric oxide.

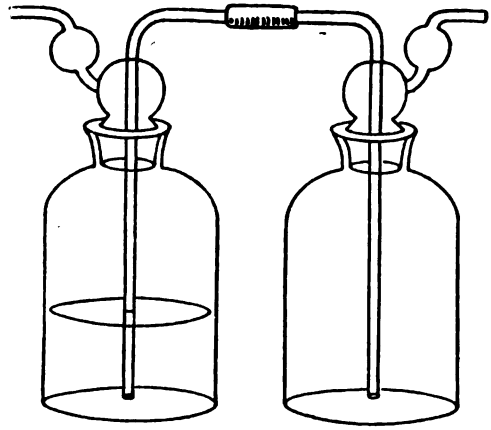

FIG. 18.

$$2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O.$$

The anhydride is led into water.

$$Cl_2O + H_2O = 2HClO.$$

The experiment is not without danger, as Cl_2O very readily explodes. The free acid is not of great importance; the salts are.

112. **Chloric acid, $HClO_3$,** is a very dangerous preparation, owing to its explosive tendencies. It is made by the cautious distillation of a mixture of strong sulphuric acid and potassium chlorate. The student is not, however, advised to attempt it, as the acid is not of much importance. A dilute solution may be made by adding the right amount of dilute sulphuric acid to a solution of barium chlorate.

113. **Perchloric acid, $HClO_4$.**—This acid is now on the market as a reagent for the quantitative determination of potassium (*q.v.* p. 206). It may be made by the careful distillation of a mixture of 50 gms. potassium perchlorate, 100 gms. sulphuric acid, and 20 c.cs. of water from a fair-sized retort.

It may also be prepared by decomposing a hot solution of potassium perchlorate by the right amount of fluosilicic acid of known strength (estimated by N NaOH). The mixture is heated for some time to complete the reaction, the precipitate of potassium fluosilicate filtered off at the pump, and the acid concentrated by evaporation at 100° C.

Should more precipitate appear, it must be filtered through a plug of asbestos, as the concentrated acid oxidises paper.

114. **Periodic acid, $HIO_4,2H_2O$ (H_5IO_6).**—Prepared *via* the sodium salt. A solution of sodium iodate and caustic soda is treated with chlorine; gradual oxidation to sparingly soluble sodium periodate takes place. The crystals are washed with a little cold water. Other periodates may be prepared by methods which will readily suggest themselves.

$$NaIO_3 + 3NaOH + Cl_2 = 2NaCl + Na_2H_3IO_6.$$

The free acid is made by treating the barium salt with the right amount of dilute sulphuric acid. See also Müller and Friedberger, *Ber.* **35** (3), 2652.

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II. Metallic Halides and Oxyhalogen Salts.

It often happens that metallic halides cannot be prepared from solution, for one of two reasons:

(*a*) Partial hydrolysis of the salt takes place, especially if required anhydrous.

(*b*) The necessary acid is not available, *e.g.* chloric, hydriodic, etc.

Hence the following methods:

115. **Anhydrous ferric chloride, $FeCl_3$.**—A hard glass tube about 25 cms. long, 1·5 cms. bore, is packed with clean iron wire 0·1 cm. diameter. The end is fitted as shown (Fig. 19) into the bottle in which the specimen is to be

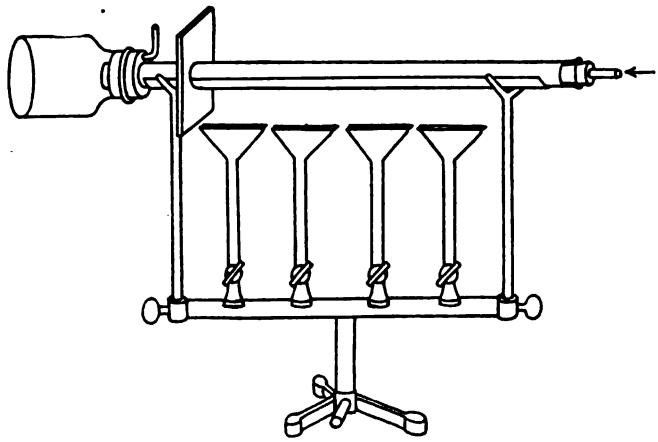

Fig. 19.

preserved, the cork being protected from the heat of the burners by an asbestos card. The iron is strongly heated in a stream of dry chlorine. Vigorous combustion occurs. Most of the product will sublime into the bottle if the temperature is high enough. Any remaining in the tube may be pushed into the bottle by means of a glass rod, after the chlorine has been swept out by a stream of air. Stopper the bottle securely whilst warm, and seal with paraffin wax.

Absolute exclusion of moisture in this and the following experiments is essential.

The part of the tube between the furnace and the bottle should be as short as possible.

Ferrous chloride may be made from the product by reducing it in a stream of hydrogen at a moderate temperature.

116. **Anhydrous aluminium chloride, $AlCl_3$.**—The apparatus is as in Fig. 19. Hydrochloric acid gas is used instead of chlorine. The tube is filled loosely with aluminium turnings, which must first be freed from oil by thoroughly washing with alcohol and drying above 100° C. The air must be completely displaced by the acid gas before heating the tube, or an explosion of hydrogen and oxygen may result. In order to prevent the stoppage of the

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tube the stream of gas must be *very rapid*. The aluminium must not be heated to melting, and moisture must be rigidly excluded.

117. **Chromic chloride, $CrCl_3$.**—This may be made by a somewhat similar method to that used for ferric chloride, with the following modifications. The tube should be shorter, and the condensing bottle is unnecessary, as the chloride is not readily volatile and will stay in the tube, in which it is sealed at the end of the experiment, after replacing the chlorine by a current of carbon dioxide. The tube is therefore drawn out at *both* ends before the experiment. The coarsely-powdered chromium obtained in No. 32 is used (10 gms.).

A mixture of $Cr_2O_3 + 3C$ may be used instead of metallic chromium. Make a paste of the required quantities of lamp-black and chromic oxide with water, roll into pellets and dry.

118. **Stannic chloride, $SnCl_4$.**—A stream of dry chlorine is led over 50 gms. of granulated tin, loosely packed in a distilling flask. Another distilling flask is fitted to the side-tube to act as receiver. The receiver should be cooled with water. A guard tube of calcium chloride excludes atmospheric moisture, and a lime tower should be attached to absorb excess of chlorine.

When no more tin will react, distil. B.P. 113·5°.

It fumes strongly in air, and with the correct amount of water forms a crystalline hydrate, $SnCl_4$, $5H_2O$, in which form it is usually sold.

It combines with ammonium chloride to form $(NH_4)_2SnCl_6$ (" pink salt "), which is used as a " mordant " in dyeing.

Antimony pentachloride, $SbCl_5$, may be similarly made. It must be distilled, however, *in vacuo*, as it decomposes under ordinary pressure at the boiling point. It boils at 78° under 20 mm. pressure.

119. **Antimony trichloride, $SbCl_3$.**—The starting-point is the mineral stibnite, Sb_2S_3. 50 gms. are finely powdered and added to excess of cold strong hydrochloric acid in a basin in the fume-cupboard. Warm gently. More acid and a *little* potassium chlorate may be added to complete solution. Boil till free from hydrogen sulphide and pour into a *large* volume of hot water. The precipitate, $Sb_4O_5Cl_2$, is washed by decantation, dissolved in strong hydrochloric acid and distilled from a retort fitted with a thermometer, using a flask, cooled under the tap, as receiver. When the temperature reaches 210°C. change the receiver. Re-distil the portion which comes over above this temperature. Seal up with a cork soaked in paraffin wax. B.P. 223°.

The first runnings may be used to prepare Sb_2O_3 (No. 18).

Antimony trioxide may be used as the raw material instead of stibnite, but it generally contains much Sb_2O_4, insoluble in hydrochloric acid.

120. **Lead tetrachloride, $PbCl_4$.** (Friedrich, *Monat. f. Chemie*, **14**, 507.)—Thoroughly grind 10 gms. of lead chloride with successive quantities of cold, strong hydrochloric acid, pouring off the liquid and the fine powder until it is all reduced to a finely divided state with about 200 c.cs. of strong hydrochloric acid. Transfer to a flask, and saturate with chlorine till almost all the chloride has dissolved. Several hours are required for this. Allow the solution to stand overnight, filter through glass-wool and cool with ice. Add an ice-cold solution of 4 gms. of ammonium chloride in 40 c.cs. of water. After some hours the yellow ammonium plumbichloride is filtered

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off, washed with ice-cold alcohol and dried at 50°. It has the composition $(NH_4)_2PbCl_6$.

To obtain the free (unstable) $PbCl_4$, it is mixed with three times its weight of ice-cold strong sulphuric acid and well stirred. After a time a heavy colourless oil separates ($PbCl_4$). It is freed from ammonium sulphate by repeated treatment with ice-cold sulphuric acid. It is not very stable, and explodes violently when strongly heated.

121. **Potassium iodide, KI.**—25 grams of pure reduced iron powder are suspended in 200 c.cs. of water in a flask, and 100 grams of iodine are slowly added, with cooling. Filter off the excess of iron, add a few more grams of iodine, and warm gently on a water-bath. Warm a 30 % solution of the required quantity of potassium carbonate, and slowly add the iron iodide solution to it, not *vice versa*. Filter and crystallise. Compare the crystals with those of the bromide and chloride.

Reaction.—Ferroso-ferric iodide is formed, Fe_3I_8, which is decomposed by the carbonate thus:

$$Fe_3I_8 + 4K_2CO_3 = Fe_3O_4 + 4CO_2 + 8KI.$$

Potassium bromide is obtained advantageously by a similar method.

122. **Anhydrous magnesium chloride, $MgCl_2$.**—Many of the *divalent* chlorides cannot be obtained pure in the anhydrous state by driving off water of crystallisation from the hydrated salt, as partial hydrolysis takes place, hydrochloric acid is evolved, and a more or less basic salt left. If, however, the dehydration is carried out in the presence of ammonium chloride, the pure anhydrous chloride is left.

Dissolve equal weights of crystallised magnesium chloride and ammonium chloride in the minimum of hot water, filter (funnel-heater !) and evaporate dry (best in platinum basin) with great care, breaking up lumps and taking precautions neither to overheat nor to leave any trace of moisture.

A test portion should not lump together when heated *gently*, nor should it evolve any moisture when heated strongly.

Transfer to a platinum crucible, and heat strongly in a gas furnace. The magnesium chloride remains as a molten mass, solidifying to radiating crystals, which should dissolve in water to form a perfectly clear solution.

Strontium chloride may be similarly prepared.

123. **Pure sodium chloride, NaCl.**—500 gms. of commercial salt are dissolved in 1500 c.cs. of boiling water in a large basin, and 15 gms. of slaked lime mixed with water are added, followed by 50 c.cs. of the bench barium chloride solution. Now add a solution of about 20 gms. of sodium carbonate, stir well and set aside.

The slaked lime causes the precipitation of the hydroxides of other metals present, especially magnesium, the barium chloride decomposes sulphates and the sodium carbonate precipitates the excess of lime and barium chloride.

The solution is filtered (avoiding disturbance of the somewhat slimy precipitate) and evaporated till the solution is practically saturated. It is then cooled and saturated with hydrochloric acid gas (using a funnel as delivery tube) and set aside overnight. Filter at the pump and dry above 100° in an air oven.

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Fine "hopper" crystals of salt are often found on the surface of the solution. These should be carefully removed and preserved.

Potassium chloride is purified in a similar manner.

124. **Cuprous chloride, Cu_2Cl_2.**—This salt is made by the reduction of cupric chloride by metallic copper.

$$CuCl_2 + Cu = Cu_2Cl_2.$$

As the salt is insoluble in water, and the copper would thus soon become coated with it, the reduction is carried out in excess of hydrochloric acid, which dissolves the chloride, forming the complex acid $H_4Cu_2Cl_6$. Moreover, it is cheaper to start from copper than from cupric chloride; the solution of the copper in the hydrochloric acid is effected by adding the right amount of nitric acid.

Twenty gms. of copper "wool" or fine turnings are added to 250 c.cs. of strong hydrochloric acid in a 600 c.c. flask. Sufficient strong nitric acid is added to convert about a quarter of the copper to copper oxide (*excess* of copper being desirable for obvious reasons).

$$3Cu + 2HNO_3 = 3CuO + H_2O + 2NO.$$

This forms cupric chloride with the hydrochloric acid, and is then reduced by the remaining copper. The solution should be warmed gently in the fume-cupboard till the first reaction has moderated, and then is well boiled till the dark green solution becomes almost colourless, more copper being added if necessary. Decant the hot liquid into a dry flask, cork up and set aside overnight. Next morning a portion of the cuprous chloride will have crystallised. This should be treated separately. The main portion is precipitated by pouring the liquid into a considerable excess of cold air-free water containing some sulphurous acid, to prevent oxidation. Allow the precipitate to settle, filter at the pump, wash three times with sulphurous acid and three times with glacial acetic acid as quickly as possible. Now dry at 100° in the open (not in an oven) so that drying is as rapid as possible. When these precautions are taken, no oxidation will take place, and the product is pure white. It does not keep well, however, absorbing oxygen to form a basic cupric salt.

Query.—Why cannot cuprous chloride, being insoluble, be prepared by double decomposition?

125. **Cuprous iodide, Cu_2I_2.**—This is, curiously, the only stable iodide of copper, and one of the most stable cuprous salts.

10 gms. of copper sulphate crystals are dissolved in water, saturated with sulphur dioxide, and the right amount of potassium iodide solution added. Allow to stand some time, filter at the pump, wash well and dry.

$$2CuSO_4 + 2KI + H_2SO_3 + H_2O = Cu_2I_2 + 2KHSO_4 + H_2SO_4.$$

The function of the sulphurous acid is to reduce the iodine set free by

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2$$

to hydriodic acid again,

$$I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4,$$

so that it can react with more copper sulphate, otherwise half the iodine is

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lost, and the reaction is, moreover, incomplete, for

$$2CuI_2 \rightleftarrows Cu_2I_2 + I_2$$

is a "balanced" action, which goes completely to the right when the free iodine is removed. (See under Volumetric estimation of copper.)

Cuprous bromide may be similarly prepared.

126. **Potassium chlorate, $KClO_3$, and chloride, KCl.**—Pass chlorine into a gently boiling 20 % solution of potash till no more is absorbed. The delivery tube should be a funnel and the solution should be in a beaker on a sand-bath. (See Fig. 20.)

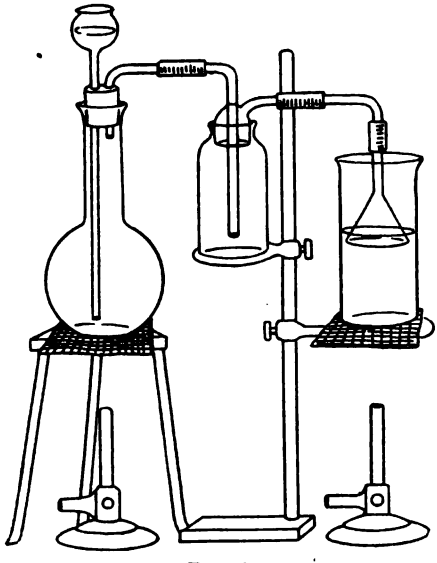

FIG. 20.

When the reaction is over transfer to a basin, boil till free from chlorine and cool rapidly with vigorous stirring. Filter off at the pump, wash once with ice-water and recrystallise the chlorate.

The liquor should be evaporated dry and strongly heated to decompose any chlorate left; it is then taken up in water and crystallised.

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

Commercially, calcium hydroxide is used, the reaction being conducted at 80° C. Potassium chloride is then added, and the chlorate formed is recrystallised.

Electrolytic methods are now replacing the above.

127. **Potassium perchlorate, $KClO_4$.**—When potassium chlorate is kept at a temperature just insufficient to cause evolution of oxygen, the following reaction takes place:

$$4KClO_3 \rightleftarrows 3KClO_4 + HCl.$$

At higher temperatures the chlorate decomposes thus: $KClO_3 = KCl + 3O$ (monomolecular change). (See Jon Scobai, *Zeit. Phys. Chem.*, xliv. p. 319 (1903).)

50 grams of chlorate are melted in a porcelain basin and kept at the necessary temperature until the mass has solidified (perchlorate has higher melting point). It is allowed to cool, ground up with a little cold water to get rid of much of the chloride. The water is poured off, and any remaining chlorate decomposed by adding a little strong hydrochloric acid and warming. (Fume-cupboard !). Cool, pour off the liquid, dissolve in the minimum of boiling water and crystallise in the usual way.

N.B.—Perbromate and periodate are *not* formed in a similar manner.

128. **Potassium bromide, KBr, and bromate, $KBrO_3$.**—To a 20 % solution of caustic potash add slowly the calculated amount of bromine. The potash solution should be titrated against standard acid, as stick potash is by no

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means pure KOH. The density of bromine being about 3, the required quantity should be measured from a burette. Set aside the product. The bromate crystallises, and should be recrystallised till free from bromide. The bromide is obtained from the mother liquor by evaporating dry with several grams of wood-charcoal and then heating strongly. The charcoal reduces the bromate, which otherwise requires a very high temperature. Allow to cool, dissolve in water, filter and crystallise. Compare the bromate crystals with those of potassium chlorate, and the bromide crystals with those of potassium chloride.

129. **Potassium iodate, KIO_3.**—This is best prepared by the action of iodine on potassium chlorate.

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

To 50 gms. of potassium chlorate in 100 c.cs. of hot water, in a large flask, add rather more than the calculated quantity of iodine (to allow for slight loss by volatilisation). To the hot mixture add a few c.cs. of hot strong nitric acid. This, after a few minutes, starts the reaction, and a torrent of chlorine, with a little iodine, is evolved. When the reaction is over, boil off the chlorine and set aside. Work up the mother liquor for another crop.

The crude product will contain some of the acid iodate (see No. 97) owing to the nitric acid which has been added. Dissolve it in hot water, and carefully neutralise with potassium *carbonate*. Recrystallise.

III. Acid Chlorides, Etc.

The "acid" chlorides are chlorides or oxychlorides which react with water to give hydrochloric acid and the oxyacid of the element in question. The most important inorganic ones are the chlorides of phosphorus and the two chlorides of sulphuric acid. The organic acid chlorides are of great importance as reagents.

The general method of preparation of an acid chloride is to treat the acid or its sodium salt with phosphorus pentachloride, by which the hydroxyl group is replaced by chlorine. This is always the method for the organic ones, but there are simpler methods for some of the inorganic ones.

In all the following preparations, careful exclusion of moisture is absolutely necessary. Moreover, it is very dangerous to inhale the vapours of any of these substances; every preparation should be done in a good draught cupboard.

The Chlorides of Phosphorus.

130. **Phosphorus trichloride, PCl_3.**—31 gms. of yellow phosphorus are cut up under water, dried as quickly as possible on some filter paper, and dropped by a pair of tongs into the retort, which is full of carbon dioxide (Fig. 21). The apparatus is fitted as shown, and a fairly rapid stream of *dry* chlorine passed over the phosphorus, which is gently heated on a sand-bath. It takes fire and fumes of the trichloride form and collect in the receiver as a liquid. Should crystals of the pentachloride form in the neck of the retort, push the chlorine tube down nearer to the phosphorus; if phosphorus sublimes, raise the chlorine tube. For this purpose it should not fit too tightly into the cork. Every care must be taken to exclude moisture. Redistil the product from a fractionating flask. B.P. 74°.

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Yield, about 120 gms. It reacts with water to form phosphorous acid

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

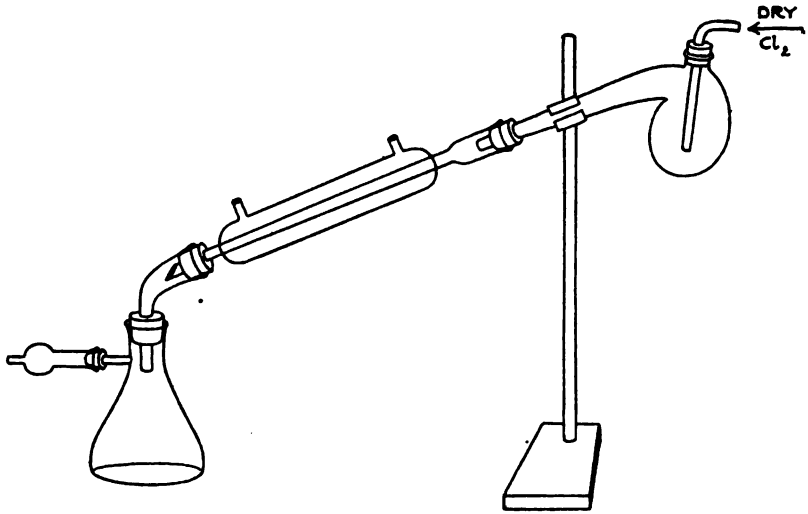

FIG. 21.

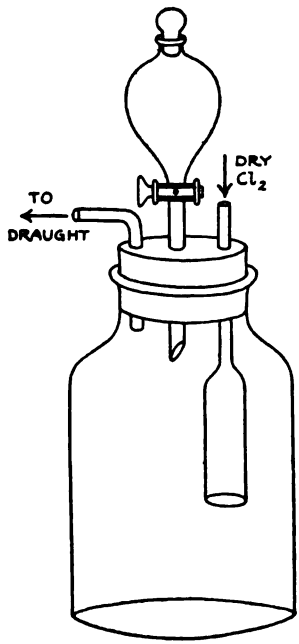

FIG. 22.

131. **Phosphorus pentachloride, PCl_5.** — The bottle in which the specimen is to be preserved is fitted as shown (Fig. 22). Chlorine is led in by the funnel, which thus prevents stoppage of the tube by the pentachloride. When the bottle is full of chlorine, phosphorus trichloride is run in, a little at a time, from the dropping funnel, waiting until the pentachloride formed appears dry between each addition. The yield is quantitative.

Reaction with water.

(1) $PCl_5 + H_2O = POCl_3 + 2HCl.$

(2) $POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$

The vapour density shows that above 290° it is completely dissociated into the trichloride and chlorine

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

(See Naumann, *Lieb. Ann.* (*Supp.*), v. 349.)

132. **Phosphorus oxychloride, $POCl_3$.** (Dervin, *Comp. Rend.*, **97**, 576.)

$$3PCl_3 + KClO_3 = 3POCl_3 + 3KCl.$$

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The required proportions of the reagents are weighed out, the chlorate is very finely powdered and added to the trichloride in the flask (Fig. 23), a

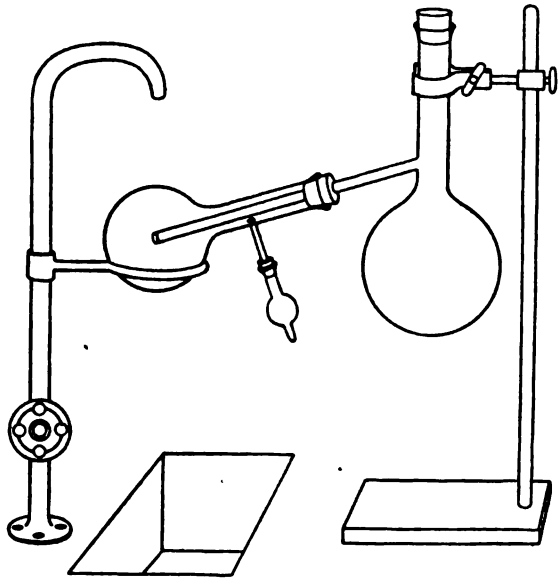

FIG. 23.

little at a time, waiting between each addition till the reaction subsides. The guard tube contains calcium chloride, to prevent ingress of atmospheric

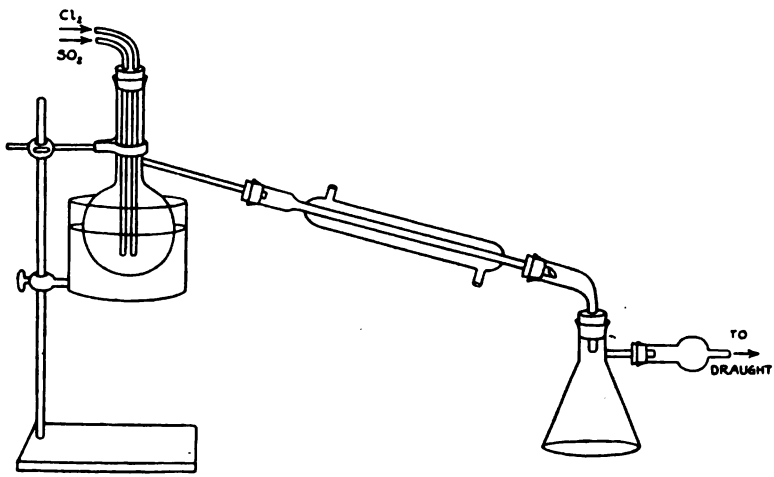

FIG. 24.

moisture. Should the action be slow in starting, warm gently. Any trichloride which distils is returned to the flask. When the chlorate has all been added, distil to dryness with a large *luminous* flame which is kept

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moving. Fractionate the product, collecting separately the portion boiling at 110°. (See also No. 135.)

133. **Sulphuryl chloride, SO_2Cl_2.**—Obtained by the direct union of sulphur dioxide and chlorine under the catalytic (?) influence of camphor (Fig. 24).

In a 500 c.c. distilling flask cooled in a vessel of water, put 50 gms. of camphor, fit up as shown, and pass in sulphur dioxide till it is no longer absorbed. Then pass dry chlorine into the liquid till it is no longer absorbed, and repeat till the volume of liquid no longer increases.

Distil the product till the temperature reaches 100°. Fractionate the distillate. B.P. of the pure chloride, 69·5°.

The residue containing the camphor may be used for another preparation.

Action with water.

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

134. **Chlorsulphonic acid, $SO_2(OH)Cl$.**—Prepare pure sulphuric acid H_2SO_4, by mixing ordinary strong acid with fuming sulphuric acid ($H_2S_2O_7$) till the density is 1·840 at 15° C.

Three molecular proportions of this are placed in a large distilling flask, and one molecular proportion of phosphorus pentachloride added gradually. The mixture gets hot, and hydrochloric acid is evolved.

Connect the flask to a distilling flask to serve as receiver (Fig. 23, p. 57), heat on an air-bath till most of the hydrochloric acid has been driven off and distil.

Fit the receiving flask with a thermometer and an air condenser (making the connections by means of asbestos paper or string; cork would be corroded). Distil again up to 165°, and fractionate the distillate. B.P. 153°.

The substance is the "half chloride" of sulphuric acid, and is used in organic chemistry as a sulphonating agent. Compare chromyl chloride and potassium chlorchromate.

135. **Thionyl chloride, $SOCl_2$** (*Lieb. Ann.*, **111**, 94).—Pass sulphur dioxide over phosphorus pentachloride in a large flask till it is all dissolved.

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$

Use at least 500 gms. of phosphorus pentachloride.

Fractionate the products and preserve them *both*. B.P. of thionyl chloride 78°. Used to prepare the esters of sulphurous acid.

Reaction with water:

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl.$$

B.P. of phosphorus oxychloride 110°.

136. **Chromyl chloride, CrO_2Cl_2.**—25 gms. of potassium bichromate are fused in a basin, allowed to cool and ground up finely, mixed intimately with 35 gms. of salt and placed in a *large* retort. Fix a fractionating flask to the neck of the retort (by a piece of rubber tubing slipped on the latter). Run 100 c.cs. of strong sulphuric acid into the retort, taking care that the whole mixture is wetted by it. Deep red fumes resembling bromine are produced. Warm gently on a sand-bath and distil. Redistil the product from the flask. B.P. 117°.

Reaction with water:

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

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137. **Potassium chlorchromate, $CrO_2(OK)Cl$.**—50 gms. of potassium dichromate are well ground with 65 c.cs. of strong hydrochloric acid, transferred to a basin, and the mixture heated on a water-bath till chlorine just begins to come off. Turn out the gas, add 70 c.cs. of hot water and allow to cool on the bath, very slowly. Fine crystals are readily obtained. The ammonium salt is similarly prepared. Note the action of water and of strong sulphuric acid.

138. **Sulphur "monochloride," S_2Cl_2.**—Pass dry chlorine rapidly (by a tube just clear of the surface) over molten sulphur in the apparatus of Fig. 23, using a distilling flask as receiver. The chloride distils as a yellow liquid, and is redistilled using an air condenser, with careful exclusion of moisture. B.P. 138° C.

Reaction with water:

$$2S_2Cl_2 + 2H_2O = 4HCl + 3S + SO_2.$$

It is used largely in the vulcanisation of rubber. It absorbs chlorine at 0°, forming SCl_2, but this dissociates again at higher temperatures. It is not a true "acid" chloride, as no corresponding acid is known.

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CHAPTER VIII.

PREPARATIONS FROM MINERALS.

139. **Strontium salts from celestine, $SrSO_4$.**—The sulphate is reduced to sulphide by heating strongly with carbon.

$$SrSO_4 + 4C = 4CO + SrS.$$

For details of the reduction see No. 14.

If desired, the hydroxide produced in No. 14 may be used to prepare the salts, but it is more economical simply to dissolve the sulphide in the required acid. This should be done in the draught cupboard.

Barium salts may by obtained from barytes, $BaSO_4$, in a precisely similar manner.

140. **Alum from cryolite, Na_3AlF_6.**—

Reaction: $$Na_3AlF_6 + 3CaO = Na_3AlO_3 + 3CaF_2.$$

Mix intimately equal weights of very finely powdered cryolite and pure quicklime. Ignite strongly in a platinum (or nickel or iron) crucible in a furnace for $\frac{3}{4}$ hour.

Grind up the product, boil with water, and test the filtrate for lime. If present, add some sodium carbonate and filter. Pass carbon dioxide through the boiling liquid till no more precipitate falls.

$$2Na_3AlO_3 + 3CO_2 + 3H_2O = 3Na_2CO_3 + 2Al(OH)_3.$$

Wash the aluminium hydroxide with boiling water (decantation), dissolve in the right amount of sulphuric acid, and add the required quantity of potassium or ammonium sulphate (calculated from the weight of cryolite taken).

The filtrate may be evaporated for pure sodium carbonate.

141. **Alum from kaolin (clay), $Al_2H_2Si_2O_8$, H_2O.**—Pure kaolin, finely powdered, is ground well with $1\frac{1}{2}$ times its weight of pure sulphuric acid. It is then gently heated on an air-bath for 3 hours. The temperature is then raised till white fumes come off thickly. Allow to cool, dissolve in water, filter, and add the calculated amount of potassium or ammonium sulphate and crystallise. (The yield of aluminium sulphate is practically quantitative.)

Manganese salts from pyrolusite, MnO_2.

142. **Manganese chloride, $MnCl_2$, $6H_2O$.**—The residual liquor from the preparation of chlorine is evaporated dry with constant stirring, ground up

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and heated gently on a sand-bath. The ferric chloride is thereby largely converted into an insoluble basic salt. Allow to cool, grind up with hot water and filter. The remaining iron is precipitated by adding manganous carbonate (obtained by precipitating $\frac{1}{12}$ of the liquid with sodium carbonate solution, filtering and washing) and boiling gently till a filtered solution is free from iron (pure flesh-coloured precipitate with ammonium sulphide). Filter and crystallise. The above method of freeing the divalent metals from iron and the trivalent metals is quite general. (See also No. 48.) The iron must, however, be in the ferric state.

143. **Potassium permanganate, $KMnO_4$.**—Mix 50 gms. of potash, 25 gms. of potassium chlorate, and a little water in a nickel basin, and heat gently till the whole is fluid. (The eyes and hands should be protected.) Now stir in 50 gms. of powdered pyrolusite, a little at a time, and then heat gently till dry, then to dull redness for some time. Remove the mass by pouring in cold water whilst it is still warm (not red hot) and grind up with a litre of water, transfer to a flask, heat (water-bath), and pass in carbon dioxide till the liquid has become a purple colour. A drop placed on a white tile should not be still green round the edges. Allow to cool and transfer to a large gas-jar. Let the muddy oxides of manganese settle, and *syphon off* the clear liquid. (It is hopeless to try to filter.) Evaporate to crystallisation, leave overnight, decant and wash with a little ice-water. Air-dry on a porous plate.

(1) $$3MnO_2 + 6KOH + KClO_3 = KCl + 3K_2MnO_4.$$

(2) $$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3.$$

On the large scale the manganese is oxidised to permanganate by ozone, thus avoiding loss of manganese. (See also No. 153.)

144. **Manganous sulphate, $MnSO_4,4H_2O$.**—Pyrolusite is very finely powdered and ground *thoroughly* to a cream with strong sulphuric acid. It is transferred to a basin and very carefully heated on a sand-bath till no more sulphuric acid fumes are evolved (350°). Finish at a barely visible red-heat in a muffle.

The ferric sulphate is thus mainly decomposed.

Extract the powdered product repeatedly with hot water and filter. Add a little manganous carbonate (see previous preparation) or a little barium carbonate, and digest at a gentle heat for some hours, till a test portion shows no iron when treated with thiocyanate. Filter and evaporate till just saturated; set aside to crystallise spontaneously.

The mother-liquor may be used for the preparation of "substituted vitriols," by adding the calculated quantity of alkali sulphate. (Solubility of $MnSO_4$ at 15° = about 26.)

145. **Potassium dichromate, $K_2Cr_2O_7$, from chromite, FeO,Cr_2O_3.**—The *very finely powdered* mineral is intimately mixed with twice its weight of potassium carbonate and one-fifth its weight of potassium nitrate, and placed in a large crucible which should not be much more than half-full. Heat in the furnace till no more carbon dioxide is evolved, and pour the fused mass into a clean sand-tray. When cold, powder and extract with several portions of boiling water. Filter. Render acid to litmus with acetic acid and neutral

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with potassium carbonate. Filter if necessary. Potassium chromate will be obtained on crystallising. If dichromate is desired, add some sulphuric acid, and concentrate.

$$2FeO, Cr_2O_3 + 4K_2CO_3 + 7O = 4K_2CrO_4 + 4CO_2 + Fe_2O_3.$$
$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2Cr_2O_7.$$

Commercially, lime is used as the alkali and atmospheric oxygen as the oxidising agent.

146. **Ammonium molybdate, $5(NH_4)_2MoO_4,7MoO_3,2H_2O$, from molybdenite, MoS_2** (Junius, *Zeit. an. Ch.*, **46**, 440; Bontrager, *Chem. News*, Feb. 2, 1900).—Molybdenite, ground to a *very fine* powder, is roasted in a basin in a muffle furnace (Fig. 5), being frequently stirred to ensure oxidation.

$$2MoS_2 + 5O_2 = 4SO_2 + 2MoO_3.$$

(The process is more quickly carried out in a combustion tube through which a stream of air is drawn by the filter pump.) The molybdic anhydride is a pale yellow crystalline substance. It is dissolved in ammonia, any unoxidised sulphide is dried and again roasted, till completely soluble (except for gangue). The solution is freed from other metals by adding a *few drops* of ammonium sulphide and leaving overnight. Filter, evaporate till saturated and add some alcohol. Set aside to crystallise. The product is air-dried.

Note the greater ease with which di-, tri- etc., salts are formed as we pass along the group from sulphur to chromium and molybdenum.

147. **Tungstic anhydride, WO_3, from wolfram, $(Fe,Mn)WO_4$.**—*Very finely* powdered wolfram is heated gently with 4 vols. of strong hydrochloric acid and 1 vol. of strong nitric acid. Yellow tungstic acid is left.

Wash by decantation, dissolve in ammonia, filter, and evaporate to crystallisation. Heat the dried crystals of ammonium tungstate very strongly in the air. Pure WO_3 is left.

148. **Vanadium compounds from vanadinite, $Pb_5(VO_4)_3Cl$.**—Warm the *very finely* powdered mineral with strong hydrochloric acid and alcohol. The vanadate is thereby reduced to V_2O_4, which forms blue "divanadyl" salts, *e.g.* $(V_2O_2)Cl_4$. Cool, filter off the lead chloride and wash with alcohol. Evaporate the blue divanadyl chloride till free from excess of hydrochloric acid, add excess of caustic soda solution and pass in chlorine. Oxidation to vanadate (V_2O_5) is thereby effected. On adding solid ammonium chloride, sparingly soluble NH_4VO_3 (meta-vanadate) is formed.

(See also Roscoe, *Ph. Tr.*, **1868**, i, **1869**, 679. Hildebrand and Ransome, *Amer. J. of Sc.*, x. 138.)

149. **Beryllium (Glucinum) salts from beryl, $3BeO,Al_2O_3,6SiO_2$** (Gibson, *J.C.S.*, **1893**, 909).—The silica is got rid of as SiF_4 by treatment with hydrofluoric acid.

50 gms. of *finely powdered* beryl are mixed in an iron basin with 300 gms. (excess) of ammonium "bifluoride" (NH_4F, HF) and 300 c.cs. of water and heated on a sand-bath. Silicon tetrafluoride is evolved. Heat to dryness (no more steam evolved), cool, grind up with a wooden pestle, and heat again till no more steam comes off. Extract with several portions of hot water, decanting each through a filter. Beryllium fluoride dissolves, alumi-

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nium fluoride does not. Evaporate, filtrate dry in a platinum basin, mix the residue with 30 gms. of strong sulphuric acid, evaporate again, and dissolve the beryllium sulphate in water. Pour it slowly, with constant stirring, into 600 c.cs. of 25 % ammonium carbonate. This precipitates any residual aluminium. Dilute to 1200 c.cs., add a few c.cs. of ammonium sulphide (to precipitate iron as sulphide), filter and evaporate to 600 c.cs. Beryllium hydroxide is thereby precipitated, and a further quantity is obtained by evaporating again. Wash and dissolve in the required acid.

150. **Lithium salts from lepidolite, petalite or spodumen** (*Lieb. Ann.*, **159**, 82).—These minerals are silicates of the felspar and mica type in which the sodium and potassium are partly replaced by lithium.

100 gms. of the *finely powdered* mineral are mixed intimately with 100 gms. of ammonium chloride and 200 gms. of marble and heated, gently for half an hour, then very strongly for one hour. Powder and extract repeatedly with boiling water and evaporate the extracts to one-eighth of their volume.

Now render the liquid alkaline with ammonia and precipitate at the boil with ammonium carbonate. Filter. The precipitate contains all calcium carbonate and a little lithium. Dissolve in acetic acid, precipitate with oxalic acid, allow to settle, syphon off the liquid and add it to the filtrate from the calcium carbonate. The lithium precipitated with the calcium is thus recovered.

Evaporate dry, expel ammonium salts by heat, moisten the cold residue with strong hydrochloric acid and dry again. The lithium chloride is extracted from this (best in a Soxhlet apparatus) by absolute alcohol, the alcohol evaporated off, the residue dissolved in water and lithium carbonate precipitated by addition of ammonia and ammonium carbonate. Wash with ammonia, dry and dissolve in required acid.

A simpler process is to fuse the mineral and pour it into water. It is thus rendered attackable by hydrochloric acid, with which the finely powdered product is repeatedly extracted. The united filtrates are evaporated dry and the lithium chloride extracted with alcohol as above.

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CHAPTER IX.

ELECTROLYTIC PREPARATIONS.

VERY many substances are now prepared electrolytically. A few of the most important only are given here. For further particulars the student is referred to *Practical Methods of Electro-Chemistry*, F. M. Perkin. (Longmans.)

The important point in electrolytic preparations is the correct **current density**, generally calculated as ampères per square decimetre of electrode.

151. **Potassium chlorate, $KClO_3$.**—Electrolyse a saturated solution of potassium chloride in a large beaker or a platinum basin. The anode *must* be platinum, the kathode may be nickel or carbon.

A *little* potassium dichromate prevents kathodic reduction.

Conditions: E.M.F., 5 volts.
Current density, 18-20 amps. per sq. dec. of anode.
Temperature, 50°-60°.

After some time the salt should commence to crystallise out. Wash once with ice-water and recrystallise.

For literature see *Jahrbuch*, 1898, p. 186; 1899, p. 198.

152. **Potassium perchlorate, $KClO_4$.**—A cold saturated solution of potassium chlorate is acidified with a few drops of dilute sulphuric acid, and a wire-gauze bag of the crystals hung at the top of the vessel to keep the solution saturated. Electrolyse under following conditions:

Temp., Below 20° (arrange to cool if necessary).
Current density, 10 amps. per sq. dec. of anode.
E.M.F., 10-15 volts.

After some time the crystals are rapidly deposited.

Potassium perbromate, $KBrO_4$, is similarly obtained from the bromate.

153. **Potassium permanganate, $KMnO_4$.**—Electrolyse a 40 % potassium carbonate solution with an anode of ferro-manganese, and an iron (or other cathode). The solution is decanted from the ferric hydrate formed at the anode. The permanganate crystallises after some time. Potassium chromate is similarly obtained by the use of a ferro-chrome anode.

154. **Potassium persulphate, $K_2S_2O_8$.**—Electrolyse a saturated solution of potassium bisulphate, employing a very small anode (about 2 mm. of thin platinum wire projecting from a glass tube). Current strength, 1 ampère, thus getting a very high current density. The anode solution should be kept separate by surrounding the anode with an open glass tube as shown, reaching

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nearly to the bottom of the vessel. The whole must be cooled with ice. (See Fig. 24.)

Ammonium persulphate is made similarly.

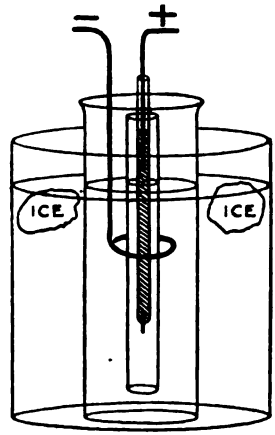

FIG. 25.

Reaction: $2HSO_4' = H_2S_2O_8$. Hence use of small anode, so that the ions can come into contact.

(For tests, etc., see p. 144).

Percarbonates and perborates are also known and are prepared similarly. (See *Compt. Rend.*, **139**, 711; **149**, 506; *Chem. Cent.*, 1905 (ii) 99. Also various years of *Ann. Rep. Ch. Soc.* since 1905.)

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CHAPTER X.

SOME SULPHUR COMPOUNDS.

BESIDES sulphur compounds and salts already described amongst general methods, there are a few important ones prepared by other methods, and also some important oxyacids of sulphur and a large class of "thio" salts which contain sulphur instead of oxygen, *e.g.* thio-carbonate, K_2CS_3; thio-antimonate, Na_3SbS_4, etc.

A. SULPHIDES.

Those of commercial importance (as pigments) are "cadmium yellow," CdS; vermilion, HgS (used instead of the expensive iodide); mosaic gold, SnS_2 (used for "bronze paint"). Also cuprous and ferrous sulphides.

General methods are:

(1) Direct synthesis.

(2) Double decomposition (hydrogen sulphide and a metallic salt).

EXAMPLES.

(1) DIRECT SYNTHESIS.

155. **Cuprous sulphide, Cu_2S.**—Copper turnings and excess of sulphur are heated in a crucible in a reducing atmosphere (hydrogen or coal-gas). For a small scale experiment a Rose crucible (see p. 195) is excellent. Heating is continued till no more sulphur vapour is evolved.

The hydrogen prevents the formation of cupric sulphide and the oxidation of the cuprous sulphide.

Cu_2S is a black, highly crystalline substance, soluble in nitric acid.

Ferrous sulphide is obtained by heating iron with excess of sulphur, but has not been obtained pure; it is prepared commercially.

156. **Mercuric sulphide, HgS** (vermilion; artificial cinnabar).—Mercury is rubbed thoroughly in a large mortar with excess of flowers of sulphur and some ammonium sulphide.

The black sulphide is obtained (as precipitated by H_2S from a mercuric salt). The product, which contains unchanged mercury and sulphur, is treated with 20 % potash and kept warm (50° on the steam oven) for several weeks.

The black variety is soluble in alkali sulphide, it dissolves, is hydrolysed slowly to the red variety, and crystallises out again, the latter being insoluble

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in alkali sulphide. The evaporated water must be replaced from time to time, and the mixture well stirred. When the colour is quite red, wash well by decantation and boil with sodium sulphite to remove any sulphur, decant and wash with boiling water and dry at 100°.

157. **Stannic sulphide, SnS_2** (Mosaic gold).—Stannous sulphide is prepared by dissolving 10 gms. of tin in 40 c.cs. of strong hydrochloric acid, diluting to 400 c.cs. and saturating with H_2S at about 80°. Filter, wash with water and dry at 100°. Mix thoroughly with half its weight of sulphur and about 5 gms. of ammonium chloride and put into a small flask. Bury it in a sand-bath, invert a small beaker over the mouth, and heat carefully till no more sulphur or ammonium chloride is evolved. The product is obtained as dull golden flakes.

(2) Double Decomposition.

158. **Cadmium sulphide, CdS** (Cadmium yellow).—Cadmium sulphate is dissolved in water, acidified with a little dilute sulphuric acid, and the solution saturated with H_2S. Filter, wash with H_2S solution and dry at 100°.

Other sulphides are similarly prepared.

B. SALTS OF THE "THIONIC" ACIDS (Debus, *J.C.S.*, 1888, p. 278).

Salts of a series of acids as follows are known, being prepared by Debus from the product of the action of hydrogen sulphide on sulphurous acid.

$H_2S_2O_6$, dithionic acid.
$H_2S_3O_6$, tri- ,, ,,
$H_2S_4O_6$, tetra- ,, ,,
$H_2S_5O_6$, penta- ,, ,,

Only the last-named is formed in any quantity by the above reaction, the others being prepared by special reactions.

Di- and tetra-thionates are the only ones of much importance to the student.

159. **Barium dithionate, BaS_2O_6, $2H_2O$.**—Very finely powdered manganese dioxide is levigated, and the coarser portions ground up again till the whole readily remains suspended in water. (*Precipitated* MnO_2 may be used without any preparation.)

50 gms. are suspended in 300 c.cs. of water in a beaker, cooled with ice, and sulphur dioxide is passed in till no more dioxide will dissolve.

$$\text{(Cold)}\quad MnO_2 + 2SO_2 = MnS_2O_6.$$
$$\text{(Warm)}\quad MnO_2 + SO_2 = MnSO_4.$$

Filter, add hot, strong baryta solution till just alkaline, pass in a little CO_2 to remove excess of baryta, filter from manganese hydroxide, barium sulphate and barium carbonate, and crystallise on a water-bath.

If the free acid is required, treat a solution of the barium salt with the exact amount of cold dilute sulphuric acid and filter. Concentrate *in vacuo*.

Reactions: Heat decomposes dithionates

$$BaS_2O_6 = SO_2 + BaSO_4.$$

The free acid readily decomposes similarly.

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160. **Sodium tetra-thionate, $Na_2S_4O_6$, $2H_2O$** (*Ber.*, 1885, p. 1871).—When sodium thio-sulphate is treated with iodine the following reaction occurs :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

The former is insoluble, the latter soluble in alcohol. Hence grind sodium thiosulphate ($5H_2O$!) with slightly more than the required amount of iodine and a *little* water till a homogeneous brown paste is obtained. Shake in a flask with alcohol, stand aside for several hours, filter at the pump and wash with alcohol till free from iodide. Recrystallise by dissolving in warm water and adding alcohol till crystallisation just begins, then set aside.

Obtain sodium iodide from the alcoholic mother-liquor.

SOME OTHER OXYACIDS OF SULPHUR.

161. **Sodium hypo-sulphite, $Na_2S_2O_4$.**—Saturate a strong solution of sodium bisulphite with sulphur dioxide. Reduce with rather more than the required quantity of zinc dust (which has been analysed for its zinc contents). The action must take place in the absence of air. This may be done by putting the liquid and the zinc into a flask fitted with a two-holed rubber stopper carrying two tubes, one just passing through the cork, the other dipping into the liquid. The air is driven out by passing a rapid stream of SO_2 for a few moments, and the flask is then closed by clips to rubber tubing attached to the two tubes. When the action is complete (leave overnight) treat the liquor with milk of lime, allow to settle, decant the clear liquor, and add salt (solid) to it. Cork up and leave. $Na_2S_2O_4$, $2H_2O$ crystallises out. Wash with acetone and dry in a desiccator.

The salt is extensively used in reducing indigo blue to indigo white in preparing the vat of dye.

On oxidation (air and moisture) it forms $Na_2S_2O_5$, H_2O, sodium "meta-bisulphite," used in photography as a preservative for developers.

$$Zn + 2NaHSO_4 + H_2SO_3 = Na_2S_2O_4 + ZnSO_3 + 2H_2O.$$

162. **Sodium thio-sulphate, $Na_2S_2O_3$, $5H_2O$.**—A solution of normal sodium sulphite is prepared by the method of No. 60. Some excess of powdered roll sulphur (*not* flowers) is added, and the whole boiled for some time in a flask, replacing evaporated water as necessary.

Reaction : $Na_2SO_3 + S = Na_2S_2O_3$.

Filter and crystallise, seeding with a fragment of the solid.

Sodium sulphite is oxidisable directly to sulphate, but if supplied with sulphur instead of oxygen it takes it up. Hence the name thio-sulphate.

Commercially it is prepared from "vat-waste" (calcium sulphides) by allowing oxidation to take place, calcium thio-sulphate being formed, which is decomposed by sodium carbonate.

C. THIO SALTS.

In which oxygen is completely replaced by sulphur. Obtained by treating metallic sulphides (thio-bases) with non-metallic sulphides (thio-acids).

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163. **Sodium thio-antimoniate, Na_3SbS_4** (Schlippe's salt).

$$3Na_2S.(9H_2O) + Sb_2S_3 + S_2(i.e.\ Sb_2S_5) = 2Na_3SbS_4 + 9H_2O.$$

Quantities of crystallised sodium sulphide, powdered stibnite and flowers of sulphur in proportions demanded by the equation are weighed out and boiled well in a basin with an equal weight of water for an hour, evaporated water being replaced frequently. Filter whilst hot, wash the residue with a *little* boiling water, add washings to filtrate, and cover up to crystallise slowly. Work up the mother-liquor. Dry the crystals on a porous plate and keep in a well-stoppered bottle.

By the action of dilute sulphuric acid on this substance, antimony penta-sulphite, Sb_2S_5, is obtained. Prepare some from the residual liquor.

164. **Potassium thio-carbonate, K_2CS_3**—A solution of potassium sulphide, K_2S, is prepared by method No. 60, using altogether 100 c.cs. of 5 % potash. Shake well for some time with 4 c.cs. of carbon disulphide. Warm on a water-bath with reflux condenser for an hour. Filter and set aside to crystallise.

The solution is used as a reagent for nickel, with which it gives a dark brown precipitate in the presence of excess of ammonia. (In dilute solution a coloration only.)

Barium tri-thio-carbonate is prepared similarly from barium sulphide (made as above) and carbon disulphide. It crystallises as a yellow powder.

165. **Potassium thio-cyanate, KSCN.**

$$KCN + S = KSCN.$$

Melt some potassium cyanide in a porcelain basin, remove the flame, and add slowly half the weight of sulphur. It dissolves with some deflagration. Allow to cool, dissolve in hot water, filter and crystallise. The salt is very soluble, and considerable evaporation is necessary. Recrystallise.

166. **Ammonium thio-cyanate, NH_4CNS.**

$$CS_2 + 2NH_3 = NH_4SCN + H_2S.$$

In a 500 c.c. strong stoppered bottle mix 50 c.cs. of carbon disulphide, 120 c.cs. of alcohol, 115 c.cs. of ·880 ammonia and 45 c.cs. of water. Tie on the stopper and stand in a warm place for some days, shaking occasionally. When the carbon disulphide has disappeared, distil off 200 c.cs. of the liquid, filter the residue whilst hot, and evaporate on a water-bath till crystals form. Cool, filter at pump, wash with alcohol and recrystallise from hot water.

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CHAPTER XI.

SOME NITROGEN COMPOUNDS.

167. **Sodium nitrite, $NaNO_2$.**—May be prepared by heating sodium nitrate strongly till no more oxygen is evolved. If a reducing agent is used, the action is carried out more quickly and easily. Lead is usually employed in the laboratory.

$$NaNO_3 + Pb = PbO + NaNO_2.$$

Fuse one molecular proportion of sodium nitrate in an iron basin (a clean sand-tray) and add gradually an atomic proportion of lead.

At a sufficiently high temperature the action takes place with deflagration and evolution of fumes (draught-cupboard). Extract the cooled and powdered mass repeatedly with boiling water, filter and pass carbon dioxide through.

Evaporate to crystallisation, cool and pour off from the small quantity of unchanged nitrate; then evaporate to dryness and extract with alcohol, in which the nitrate is insoluble. Distil off the alcohol and recrystallise the nitrate.

Potassium nitrite may be similarly prepared.

168. **Hydroxylamine sulphate, $(NH_2OH)_2H_2SO_4$** (*Tr. C.S.* (1896), p. 1665). —Nitrous acid and sodium bisulphite react thus:

$$HON : O + \begin{matrix} H & SO_3Na \\ H & SO_3Na \end{matrix} = H_2O + HO . N(SO_3Na)_2$$

forming oximido-sulphonate. This is hydrolysed at 90° thus:

$$HO.N(SO_3Na)_2 + 2H_2O = HONH_2 + 2NaHSO_4.$$

Dissolve one molecular proportion each of sodium nitrite and sodium carbonate in the minimum of cold water and cool in ice and salt; pass in sulphur dioxide till acid. Now add a few drops of sulphuric acid and keep at 90° for about 48 hours. The change is complete when a test portion freed from sulphate by *excess* of barium chloride and filtered gives no further precipitate on boiling.

Neutralise with sodium carbonate, evaporate somewhat and cool in ice and brine. Sodium sulphate crystallises. Filter and evaporate till on cooling a good yield of crystals is obtained. Treat the mother-liquor as before for a second crop. Recrystallise the whole.

Hydroxylamine is a strong reducing agent. Try the action of it on salts of mercury, copper, etc., in both acid and alkaline solution.

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It possesses one oxidising action, viz., ferrous hydrate in *alkaline* solution is oxidised to ferric hydrate.

$$NH_2OH + 2Fe(OH)_2 + H_2O = 2Fe(OH)_3 + NH_3.$$

In *acid* solution, however, ferric salts are reduced.

169. **Hydrazine sulphate $(N_2H_4)_2H_2SO_4$** (Raschig, *German patent*, 198307).—This method depends on the formation of monochloramine when ammonia is treated with a hypochlorite,

$$NH_3 + NaClO = NaOH + HN_2Cl,$$

and its reaction with more ammonia,

$$NH_2Cl + NH_3 = (N_2H_4)HCl.$$

The oxidation of ammonia by the hypochlorite to nitrogen and water is retarded by the addition of glue.

The sodium hypochlorite is prepared by passing chlorine into caustic soda solution (1 part of soda in 2 parts of water) cooled with ice. Excess of chlorine must be avoided. The solution thus prepared is added to a considerable excess of ammonia solution of S.G. 0·94 with which 1-2 c.cs. of liquid glue have been thoroughly mixed. (Use about ten times the calculated quantity of ammonia; the above solution contains 16 % NH_3 approximately.) The solution is heated rapidly to boiling in a large flask in the draught-cupboard. Remove the burner if the mixture threatens to froth over. Evaporate till the smell of ammonia disappears and the solution is about one-third of its original volume. Filter (if necessary) whilst hot, cool, add 10 c.cs. of strong sulphuric acid for every 100 c.cs. of solution, and cool with ice. Filter off the crystals at the pump. Recrystallise from the minimum of boiling water, cooling, adding strong sulphuric, and ice-cooling as before. Finally wash with alcohol, ether and dry on a filter-paper.

Hydrazine is a powerful reducing agent. Try its action on solutions of copper, silver, mercury, gold, ferric salts.

An alternative but less convenient preparation is as follows: (*B.* **28**, 2374)

$$HCN + 2KHSO_3 = H(NH_2)C(SO_3K)_2 \text{ (Amino-methane-disulphonate).}$$

On acidifying, the acid salt

$$H(NH_2)C(SO_3H)(SO_3K)$$

is obtained, which by treatment with potassium nitrite reacts thus:

$$H(NH_2)C(SO_3H)(SO_3K) + KNO_2 = 2H_2O + \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>C(SO_3K)_2$$

diazo-methane disulphonate.

This adds on sulphurous acid at the double bond, giving

$$\begin{matrix} H.N \\ | \\ HSO_3-N \end{matrix}\!\!>C(SO_3K)_2,$$

which on hydrolysis forms $(N_2H_4) + CO_2 + 2SO_2 + H_2SO_4$.

Dissolve 75 gms. of potash in 300 c.cs. of water. Saturate with sulphur dioxide. Gradually add to the product 50 gms. of powdered potassium

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cyanide with constant shaking. When dissolved heat on the water-bath, and keep the reaction acid by continually adding small quantities of hydrochloric acid till no more is required upon further heating. Then add 150 c.cs. of strong hydrochloric acid and cool in ice. Filter off the amino compound, wash with a little ice-water, and grind to a paste with water. Add a solution of 10 gms. of potassium nitrite in 6 c.cs. of water. Keep the temperature at 45° till all has dissolved, render alkaline with potash and cool. Filter off the diazo-body and dry between filter-paper under pressure. Treat it with its own weight of crystallised sodium sulphite in twice its weight of water. When dissolved render alkaline with caustic soda, warm gently for a time, and then hydrolyse the product by adding a considerable volume of 20 % sulphuric acid and setting aside. When no more sulphur dioxide is evolved, filter and cool on ice. Filter off the hydrazine sulphate, evaporate the liquor for a further crop, and recrystallise the whole from dilute sulphuric acid as before.

Hydrazine may also be prepared from organic sources.

170. **Ammonium carbamate, $NH_4 . CO . NH_2$.**—Dry ammonia gas and dry carbon dioxide are passed simultaneously into absolute alcohol (or methylated spirit that has been distilled from quick-lime). *Wide* delivery tubes should be used, or the crystalline product will stop them up. Approximately two volumes of ammonia and one of carbon dioxide should be used, and the vessel should be cooled with water.

$$C\begin{cases}O\\O\end{cases} + \begin{matrix}NH_3\\NH_3\end{matrix} = C\begin{cases}NH_2\\O\\ONH_4\end{cases}$$

After a short time a thick mass of small crystals is formed. Filter at the pump and dry in the air.

Commercial ammonium carbonate is a mixture of bicarbonate and carbamate. When the carbamate is dissolved in water and heated it is hydrolysed to the carbonate.

$$NH_4CONH_2 + H_2O = (NH_4)_2CO_3.$$

Reactions: (1) Calcium carbamate is soluble in water. Hence add calcium chloride solution to the carbamate. Filter off any calcium carbonate and heat the filtrate. Calcium carbonate is formed by hydrolysis of the carbamate, and is precipitated.

(2) Bromine water oxidises it, with production of nitrogen.

(3) Nitrous acid reacts with it, producing nitrogen.

$$CO\begin{cases}NH_2 + O:N.OH\\ONH_4\end{cases} = C\begin{cases}OH\\O\\ONH_4\end{cases} + N_2 + H_2O.$$

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CHAPTER XII.

COLLOIDS.

For a summary of the properties of colloids see Friend's *Text-book of Inorganic Chemistry* (Griffin), Vol. I., pp. 78-86, 3rd. ed.

PREPARATION OF COLLOIDAL SOLUTIONS.

A. ACIDS, BASES, SALTS.

171. **Silicic acid hydrosol (Kühn).**—A 3 % solution of water-glass is poured into rather more hydrochloric acid of density 1·1 than is required to react with it. The slight excess of acid is neutralised by the further careful addition of water-glass. The product may be purified by either of the following methods :

(*a*) Dialyse it (best by a sausage-skin dialyser, which offers a large surface, or else by making a bag of parchment paper tied round a bottle neck).

The dialyser is hung in a large vessel of water, the solution poured into it, and water is slowly run through the vessel till the runnings no longer react with silver nitrate. Concentrate to 6 % silicic acid.

(*b*) Warm to 25° when gel-formation takes place. Wash free from salt on a cotton filter, and boil for 12 hours with pure water, when only a small residue will be left. Allow to settle, decant and concentrate to 6 % silicic acid.

172. **Ferric hydroxide hydrosol.**—Boil a 3 % solution of ferric chloride for some time. Dialyse the deep-brown liquid till free from HCl.

173. **Tungstic acid hydrosol.**—Add a 5 % solution of sodium tungstate to exactly the right quantity of dilute hydrochloric acid. Dialyse till free from acid. This sol is very stable and may be evaporated to dryness (care not to overheat !) and redissolved to a hydrosol.

174. **Arsenious sulphide hydrosol.**—Shake arsenious oxide with distilled water. Filter. Pass hydrogen sulphide. Filter if necessary and remove excess of H_2S by a stream of pure CO_2-free air.

B. METALS BY REDUCTION.

175. **Gold hydrosol** (Zsigmondy).—·06 gms. of $HAuCl_3$ in 100 c.cs. of water is treated with 3 c.cs. of N . K_2CO_3 and just raised to the boil. Remove the

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flame and quickly add *dropwise* 4 c.cs. of 1 % formaldehyde, stirring vigorously all the time.

Differently coloured sols may be obtained by using other reducing agents as hydrazine hydrate, hydroxylamine, hypophosphorous acid, etc.

176. **Silver hydrosol** ("Argyrol," etc.).—Dilute silver nitrate solution is reduced by a cold 15 % solution of ferrous sulphate and 40 % sodium citrate solution. The blue ppt. is washed, filtered off and on treatment with water it gives a blue hydrosol.

Very dilute hydrazine, etc., may also be used as the reducing agent.

C. ELECTRICAL METHODS (BREDIG).

177. **Platinum hydrosol.**—An arc is struck under water in a porcelain basin between two stout platinum wires. Current 7-10 amps. at 50-70 volts. Filter off the coarser particles. A brown solution is obtained which is a very active catalyst.

Other metallic sols may be similarly obtained. Some metals give better results if a *trace* of alkali be added to the water.

178. **Illustrations of general properties of sols.**

(*a*) *The Brownian movement.*—Examine a drop of As_2S_3 (etc.) hydrosol under a microscope ($\frac{1}{8}$ in. objective). Note the jumping movements of the particles (which must be smaller than ·003 mm. to show the movement).

(*b*) *Gel formation.*—To some As_2S_3 hydrosol add a few drops of any electrolyte, *e.g.* HCl solution. Note the coagulation.

(*c*) *Cataphoresis.*—Place some As_2S_3 hydrosol in a V-shaped tube about 20 cms. long, and pass an electric current at 60 volts between platinum electrodes. Note the movement of the sol to the anode, showing it to be negatively charged.

Repeat with ferric hydroxide sol or a bismuth sol (Bredig's preparation). The disperse phase moves to the kathode, showing it to be positively charged. (Picton and Linder.)

(*d*) *Mutual pptn. of two sols.*—If a positive sol is added to a negative sol, they mutually discharge and ppt. one another. Try As_2S_3 and $Fe(OH)_3$.

(*e*) *Action of electrolytes.*—It is found that the gel formation of sols is caused by the ion of opposite charge to that on the sol. *A definite amount of this ion is contained in the gel ppt.* as might be expected.

Try As_2S_3 and a little $BaCl_2$ solution. The solution becomes acid owing to some barium ions being carried down by the gel. (Picton and Linder.)

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BOOK II.

QUALITATIVE ANALYSIS (INORGANIC).

CHAPTER I.

INTRODUCTION AND THEORY.

It is the author's firm conviction that qualitative analysis is the best method of assimilating the facts and principles of inorganic chemistry; certainly the chemistry of the metals. Owing, however, to the necessity of reducing it to a strict routine, it has tended to become mechanical. The use of "tables" has, of course, been largely responsible for this; nevertheless, tables have been given here, for tables constructed by the student not only consume much time that cannot well be spared, but are generally not altogether satisfactory.

It cannot be too strongly urged upon the student, however, that a thorough understanding of the principles employed is absolutely necessary; and an attempt, at any rate, may be made to construct a given table from a consideration of the reactions which have been studied and are to be used. It should also be remembered that the object of learning analysis is *not*, from the student's point of view, to be able to "spot" the largest number of substances in the shortest time, but is to acquire a knowledge of inorganic chemistry. Finally, absolute cleanliness is again insisted upon; an untidy worker is never so hopelessly confused as he will be over qualitative analysis.

Theoretical considerations.—The great majority of inorganic substances are classed as acids, bases or salts. These show by their properties, both physical and chemical, that they are composed of two parts called *radicals*, or (in solution) *ions*, one of which (the metal of a base or salt and the hydrogen of an acid) is electro-positive, and the other (the remainder of an acid or salt and the hydroxyl of a base) electro-negative.

A given acid and its salts show certain properties in common, which are attributable to the presence of the same radical in them all: *e.g.* (SO_4) in sulphuric acid and sulphates; (NO_3) in nitric acid and nitrates, etc.

Generally speaking, qualitative analysis consists in the *recognition of these radicals*; *not of separate elements*. This is accomplished by causing the radicals to form characteristic compounds, recognised by their insolubility, colour, or both. Thus any soluble sulphate forms white insoluble barium

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sulphate when barium ions (as barium chloride solution) are added to it. The substance added to recognise a given radical is called the reagent for that radical.

Now there are great differences in solubility even amongst "insoluble" substances. No substance is absolutely insoluble in water, and hence there is a limit of dilution beyond which a given radical cannot be detected by a given reagent. Thus lead chloride is appreciably soluble in cold water. The dissolved portion is ionised thus:

$$PbCl_2 \rightleftarrows Pb^{\cdot\cdot} + 2Cl'.$$

In the case of "insoluble" substances, the solution will be so dilute that practically all the dissolved substance is ionised. If now we increase the concentration of either of the ions, the reaction will proceed from right to left in accordance with the Mass Law, and more of the associated substance will be produced. As, however, the solution is already saturated with this substance, addition of excess of one of the ions (*i.e.* excess of the reagent) will, *caeteris paribus*, have the effect of making the substance less soluble and the reaction more delicate.

Generally, if $$A \rightleftarrows B^{\cdot} + C',$$

and if a is the concentration (mols. per litre) of A,
" b " " " " " B,
" c " " " " " C,

then $\frac{b \cdot c}{a}$ = a constant (at a given temperature).

When a has the value of the solubility of A, the solution will be saturated; if $a >$ solubility of A, then A will be precipitated. The product $b \cdot c$ is called the "solubility product." Obviously increase of b or c (the ions) causes increase in a; hence we see the reason for a precipitation being more complete on adding excess of the reagent. The reasoning applies equally to "soluble" substances. If hydrochloric acid be added to a saturated salt solution (*i.e.* the concentration of the Cl ions is increased), then the concentration of the associated NaCl is increased, and some is precipitated. (See p. 52.)

Many reagents give similar reactions with several radicals, and hence several tests must be applied to distinguish them; we take advantage of this fact, however, viz. that a few common reagents react similarly with certain radicals (especially the metals) to effect a preliminary separation of these radicals into "groups." We then find which member of the group is present by other tests. These tests, being made in solution, are called "wet" tests.

There are, however, several important tests carried out on the dry substance which are of great importance and interest and are usually performed first. These are:

(1) Action of heat on the substance (not useful with mixtures).

(2) Reduction to metallic oxide or metal (if possible), either on a "charcoal stick" or on charcoal with the mouth blowpipe.

(3) Borax bead tests.

(4) Flame tests.

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(5) Bunsen's "flash" tests, in which a film of the metal or oxide is deposited on a white glazed basin and subjected to reactions.

(These five are largely tests for the positive (metal) radicals).

(6) Action of dilute hydrochloric acid on the dry substance,

(7) Action of strong sulphuric acid on the dry substance,

are obviously for the purpose of obtaining the acid (if volatile) or its decomposition products (if any), and thus recognising the acid radical.

In conducting an analysis these preliminary tests, *or such of them as are found to be necessary*, are performed in the above order. The results are described under each metal or acid, *and should be tabulated* in a notebook by the student for his own use.

The method of carrying out each test is now described.

1. **The action of heat.**—A little of the powdered substance is heated in a small bulb blown on one end of a piece of *hard* glass-tubing about 60 × 5 mms. This test often gives an idea of the acid and sometimes of the base. Tabulated results from your own experiments are of value, as reference is facilitated.

E.g. *Observation.*	*Conclusion.*
A gas is evolved.	
(*a*) Colourless.	
(1) Turns lime-water milky.	CO_2 from a carbonate.
(2) Re-kindles a glowing splinter.	O_2 from peroxides, some oxides, chlorates, some nitrates, etc.
(*b*) Coloured. Brown (NO_2), etc.	Nitrates or nitrites of many metals.

It is not proposed to enter into detail in this test, as most of the reactions will be well known to a comparative beginner, and others can be found in the following pages.

2. **Reduction by charcoal.**—A shallow hole the size of a sixpence is scooped near one end of a block of charcoal. The substance is placed in this and

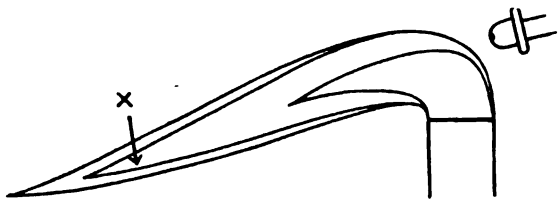

FIG. 26.

heated in the reducing flame of a mouth blowpipe. This flame is produced by holding the blowpipe nozzle just outside the luminous flame of the bunsen, and blowing gently. It should be a pointed luminous flame, and the substance should be heated about the point marked *X* in the figure.

The attachment to the bunsen may be used if preferred, but is unnecessary. Many compounds are thus reduced to the metal or to the oxide, both of which are often characteristic.

Should difficulty be experienced in obtaining a bead of metal (indications of tiny beads are seen), mix the powdered substance with several times its

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bulk of "fusion mixture" ($Na_2CO_3 + K_2CO_3$ in molar proportions: lower melting point then either alone) and heat again. The metal is thereby converted to its carbonate, which by loss of carbon dioxide leaves the oxide, which, if reducible, is then reduced to metal.

If in this test a white infusible residue is obtained, luminous when hot, a drop of cobalt nitrate solution is put on it, and the mass heated very strongly in the oxidising flame (nozzle in flame, blow harder). (Fig. 27.)

Oxides of zinc, aluminium and magnesium form characteristically coloured masses when thus treated.

The charcoal stick reduction is useful, as it can be carried out with a minute quantity of the substance.

Melt a crystal of washing soda and soak in the liquid a large round match-stalk, then burn it in the bunsen till a small stick of charcoal attached to a handle is left. If the match is well soaked with soda the charcoal will not easily burn away. A small quantity of the substance is now made into a paste with a little of the molten soda, carefully taken up on the end of the charcoal stick, and heated in the lower reducing flame of the bunsen (see Fig. 28), finally being cooled off in the gas at the base of the flame. It is then crushed in a small agate or glass mortar, and the charcoal washed away by a gentle stream of water. Any metallic beads or particles produced can then be examined and tested by the usual reactions.

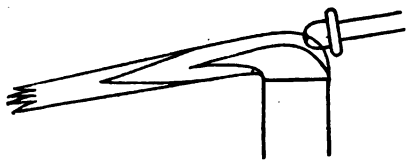

FIG. 27.

If a black or coloured residue is left on the charcoal block, apply the

3. **Borax bead test**, depending on the colours produced when compounds of certain metals (most of those whose *oxides* are coloured) are fused with borax.

A clean platinum wire is heated and dipped into borax powder. (A loop may be made on the end of the wire if preferred, by bending it carefully round a piece of stout wire or thin glass tubing). The borax is then heated till it fuses to a clear bead. A minute quantity of the substance is then taken up on the bead and fused into it by the mouth blowpipe flame, using both oxidising and reducing flames. Allow to cool and note the colour of the bead (see under each metal). Tabulate results.

N.B.—A black bead means that too much of the substance has been used.

The wire is cleaned by melting the bead, detaching it by a gentle jerk, fusing another portion of borax, shaking that off, and heating strongly till the sodium flame disappears.

4. **Flame tests.**—A little of the substance, moistened with dilute hydrochloric acid, is heated on a platinum wire in the non-luminous bunsen flame. If a "reducible" metal (Pb, Sb, Bi, Sb, As, Ag, Cu, Sn) is present, an asbestos thread must be used, as the metal will alloy with the platinum and spoil the wire.

Only *volatile* compounds of the metals will colour the flame. The chloride is the most volatile salt as a rule. Hence moisten the substance with dilute hydrochloric acid first.

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If a metal spatula carrying a pinch of ammonium chloride is held in the flame near the base, and the platinum wire just above it, the flame test is readily obtained, for ammonium chloride vapour dissociates into ammonia and hydrochloric acid, and the substance is therefore heated in hydrochloric acid gas.

Metals of the alkalis, alkaline earths, and a few other substances impart characteristic colours to the flame. The spectrum of the flame may be examined (a pocket spectroscope is useful).

5. **"Flash" tests.**—The air-holes of the bunsen (which must be fitted with a draught shield as shown) are regulated till the tip of the inner cone just becomes luminous. The structure of the flame is shown in Fig. 28.

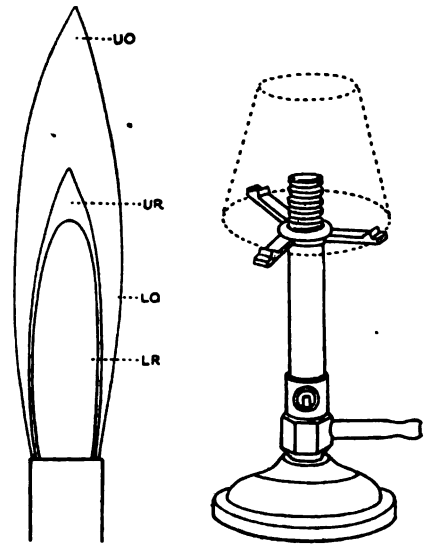

FIG. 28.

UO. Upper oxidising flame; UR. Upper reducing flame; LO. Hottest part and lower oxidising flame; LR. Lower reducing flame.

A reducible metallic oxide (or salt which is reducible by the flame gases) held on an asbestos thread at UR, is reduced to metal, which (if volatile) burns again to oxide at UO. A film of a volatile metal or its oxide can therefore be deposited on a *glazed* basin full of cold water held at UR (just above the asbestos) or at UO respectively. Reactions can be performed with these films by changing the *oxide* film to the *iodide* (by heating with hydriodic acid; an asbestos pad attached to a platinum wire is dipped in alcoholic iodine solution, ignited and the flame allowed to play on the film; then heat very gently to drive off any free iodine). Hydrogen sulphide or ammonium sulphide vapour can be blown on to this iodide film (by a small reversed wash-bottle), and the sulphide recognised.

The following metals give films of metal or oxide: Bi, Sb, As; Zn and Cd give oxide films only.

It should be noted that this is a very useful confirmatory test for a *small quantity* of precipitate obtained in the course of analysis.

Reactions 6 and 7, with hydrochloric and sulphuric acids respectively, are performed in test-tubes. About as much substance as will cover a sixpence is placed in the tube, the acid added, and if there is no action, gently warmed.

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CHAPTER II.

DETECTION AND SEPARATION OF THE POSITIVE RADICALS (KATIONS).

Division of Metals (Kations) into Groups.

It has already been mentioned that several common reagents react similarly with several metals. Advantage is taken of this to secure a preliminary separation. The groups are as follows:

Group I. contains those metals whose chlorides are insoluble (or practically so) in dilute acids. They may therefore be precipitated by *dilute hydrochloric acid.*

Group II. contains the remaining metals, whose chlorides are soluble, but whose sulphides are insoluble, in dilute acids. They are therefore precipitated *from acid solutions by hydrogen sulphide.*

Group III. contains the remaining metals whose sulphides are soluble in dilute acids, but insoluble in water or alkaline solutions; also those metals whose sulphides are hydrolysed into hydrogen sulphide and metal hydroxide. They are therefore precipitated by *hydrogen sulphide from ammoniacal solutions* either as sulphide or hydroxide.

Group IV. contains the remaining metals whose sulphides are soluble in water, but whose carbonates are insoluble in ammonium salts. They are therefore precipitated by *ammonium carbonate in the presence of ammonium chloride and ammonia.*

Group V. contains the remaining metals, which are not precipitated by any of the above reagents, and have *no group reagent* in common.

It is obvious that the above reagents will not always tell us what metals are present in the substance being examined, but will only confine us to several of a given group. To complete an analysis, confirmatory tests for each metal separately are necessary. The principal reactions of each metal will now be studied; the manner of applying these to mixtures, etc., will be considered later.

The principal confirmatory reagents in use, besides the group reagents, are as follows:

Sodium (or potassium) hydroxide.—This ppts. the metallic hydroxides (or oxides) which are generally very characteristic. In the following pages, wherever potash is used, soda will do instead, and *vice versa*, unless it is specially stated otherwise.

Ammonium hydroxide.—This generally does *not* ppt. the hydroxide simply,

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the reaction often being complex, but still characteristic. In the case of the trivalent metals, however, the hydroxides are pptd.

Sodium (or potassium) carbonate (not ammonium).—The carbonates or basic carbonates are not nearly so characteristic as the hydroxides, many being white.

Sodium phosphate.—A similar remark to the foregoing applies to this reagent, many of the phosphates being of similar appearance (white).

Potassium chromate ppts. a few characteristic chromates.

Potassium iodide ppts. a few characteristic iodides.

These are the more common reagents; there are, in addition, a large number of reagents which are used for one or two metals only.

The solutions of all reagents should be of known strengths, and the student should endeavour throughout to use the reagents in reasonably accurate quantities. If reagents of unknown strength are used in any proportion, success cannot be expected. Always employ approximately known quantities of substances and act on them with known quantities of reagents. Solutions are made containing a known weight of the reagent per litre. A solution containing one gram-equivalent of the reagent per litre is called a **normal** solution. Other strengths are referred to as multiples or sub-multiples of this. Thus we always know how much of one solution to take to react with another.

I. *Strong Acids.*—As purchased, these are approximately:

Hydrochloric -	33 %	Average. For exact strengths consult specific gravity tables of each acid.
Sulphuric -	97 %	
Nitric - -	70 %	

The following dilutions are not sufficiently exact for quantitative work, but will be found quite accurate enough for qualitative reactions.

II. *Dilute Acids.*

Hydrochloric -	4N, 1 vol.	strong acid : 1½ vols. water.
Sulphuric -	4N, 1 ,,	,, ,, : 9 ,, ,,
Nitric - -	4N, 1 ,,	,, ,, : 3 ,, ,,
Acetic - -	4N, 1 ,,	glacial acetic acid : 3½ vols. water.

III. *Alkalis.*

Sodium hydroxide, 4N.—Dissolve 1 lb. in 2700 c.cs. of water. Allow impurities to settle, and decant into a clean stock-bottle.

Potassium hydroxide, 4N.—Dissolve 1 lb. in 2000 c.cs. of water and treat as above.

Ammonium hydroxide, 4N.—1 vol. ·880 ammonia : 4 vols. water.

(·880 ammonia contains 35 % of NH_3.)

IV. *Salts.*

Ammonium chloride, 4N.—214 gms. per litre of solution.

Ammonium carbonate, 4N.—320 gms. of the commercial substance, 175 c.cs., ·880 ammonia; dilute with water to 2 litres.

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Sodium carbonate, 2N.—106 gms. of the anhydrous salt per litre of solution.

Sodium hypochlorite, 2N.—Saturate 4N caustic soda with chlorine.

Ammonium sulphide.—Use as purchased. It is about 10 normal; it decomposes gradually, losing NH_3 and forming $(NH_4)_2Sx$.

The following are all **normal.** A litre of solution contains:

Barium chloride	$BaCl_2, 2H_2O$	122 gms.
Sodium phosphate	$Na_2HPO_4, 12H_2O$	120 ,,
Potassium ferrocyanide	$K_4Fe(CN)_6, 3H_2O$	106 ,,
*Ferrous sulphate	$FeSO_4, 7H_2O$	139 ,,
Lead acetate	$Pb(C_2H_3O_2)_2, 3H_2O$	190 ,,
Ammonium oxalate	$(NH_4)_2C_2O_4, H_2O$	71 ,,
Stannous chloride	$SnCl_2, 2H_2O$	113 ,,
Potassium chromate	K_2CrO_4	194 ,,
†Potassium dichromate	$K_2Cr_2O_7$	49 ,,
Calcium chloride	$CaCl_2, 6H_2O$	110 ,,
Ferric chloride	$FeCl_3, 6H_2O$	135 ,,
Sodium thio-sulphate	$Na_2S_2O_3, 5H_2O$	248 ,,
Potassium cyanide	KCN	66 ,,

The following are **semi-normal.** A litre of solution contains:

Cobalt nitrate	$CO(NO_3)_2, 6H_2O$	123 gms.
Potassium iodide	KI	83 ,,
,, thio-cyanate	$KCNS$	50 ,,
Copper sulphate	$CuSO_4, 5H_2O$	63 ,,
‡Mercurous nitrate	$Hg_2(NO_3)_2$	132 ,,

The following are **deci-normal.** A litre of solution contains:

Silver nitrate	$AgNO_3$	17 gms.
†Potassium permanganate	$KMnO_4$	3·16 gms.
Uranyl acetate	$(UO_2)(C_2H_3O_2)_2, 2H_2O$.	21·28 ,,

The following solutions are used saturated:

Hydrogen sulphide, H_2S. (Will not keep.)

Barium hydroxide, $Ba(OH)_2$.—Used as suspension in saturated solution, baryta "milk."

Calcium hydroxide, $Ca(OH)_2$.—Also used sometimes as "milk of lime."

Calcium sulphate, $CaSO_4, 2H_2O$.—About 2·6 gms. per litre.

Bromine water.—About 36·6 gms. per litre.

Ammonium acetate.

Sodium hydrogen tartrate.

Sodium picrate (containing some sodium carbonate).

* To prevent oxidation the solution must be made in air-free water containing a little sulphuric acid, and the bottle well stoppered.

† *I.e.* with reference to available oxygen.

‡ Hydrolysed by water. Dissolve in very dilute nitric acid.

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GROUP I.

Group reagent, HCl.

SILVER, LEAD, MERCURY(-OUS) [THALLIUM].

SILVER, Ag = 107·88.

DRY TESTS.

On charcoal with sodium carbonate in the reducing flame a bead of silver is easily obtained; no incrustation. The bead is harder than lead, malleable, but does not mark paper. It dissolves in dilute nitric acid (difference from tin).

A similar bead is obtained on the charcoal stick.

WET TESTS.

Use an aqueous solution of silver nitrate.

1. **HCl** or soluble chlorides ppt. white curdy silver chloride, AgCl, insoluble in dilute acids, soluble in ammonia, forming $AgNH_3Cl$.
2. **KOH** ppts. dark brown silver oxide, Ag_2O (the hydroxide is unknown).
3. **NH_4OH** also ppts. Ag_2O, easily soluble in excess of the reagent.
4. **K_2CrO_4** ppts. dark red silver chromate, Ag_2CrO_4, soluble in dilute acids. The dichromate ppts. silver dichromate similar in appearance.
5. **H_2S** ppts. black silver sulphide, Ag_2S, insoluble in ammonia and alkali sulphides, but easily soluble in hot dilute nitric acid.
6. **Na_2CO_3** ppts. white silver carbonate, Ag_2CO_3, becoming yellow on boiling, owing to slight decomposition into the oxide and carbon dioxide.
7. **KCN** ppts. white AgCN, insoluble in dilute nitric acid, readily soluble in excess of the reagent, forming $K[Ag(CN)_2]$, and in ammonia.

Other silver salts will be found under various acids. They are not used as reactions for silver, but for the acids in question.

LEAD, Pb = 206·9.

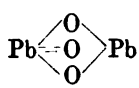
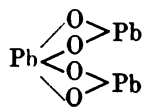
Most lead salts are those of the oxide PbO. A few are known in which PbO_2 functions as a basic anhydride, *e.g.* $PbCl_4$ (p. 51). PbO_2 more commonly figures as an acid anhydride. Calcium plumbate is well known (p. 16), and the oxides Pb_2O_3 and Pb_3O_4 are to be regarded as the lead salts of plumbic acid, owing to their reaction with acids. Thus:

$$Pb_2O_3 + 2HNO_3 = H_2O + Pb(NO_2)_2 + PbO_2.$$

Cf. $$PbCO_3 + 2HNO_3 = H_2O + Pb(NO_3)_2 + CO_2,$$

and $$Pb_3O_4 + 4HNO_3 = 2H_2O + 2Pb(NO_3) + PbO_2.$$

These two oxides therefore figure respectively as:


lead plumbate and

lead ortho-plumbate.

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N.B.—With hydrochloric acid both yield chlorine, the peroxide liberated acting at once as an oxidising agent.

$$PbO_2 + 4HCl = 2H_2O + PbCl_2 + Cl_2.$$

Dry Tests.

On charcoal all lead compounds readily yield a bead of lead, with a *yellow incrustation* (p. 77); some require to be mixed with fusion mixture, *e.g.* PbS, $PbCl_2$. The charcoal stick also readily yields a bead. The lead bead is very malleable and marks paper. Dilute nitric acid is the proper solvent for lead. Strong nitric acid has scarcely any action, owing to the insolubility of the nitrate in nitric acid. For a similar reason, strong hydrochloric and sulphuric acids scarcely act on lead in the cold, but when heated, the protecting coat of chloride or sulphate becomes soluble in the acid, forming $PbHCl_3$ and $Pb(HSO_4)_2$.

Wet Tests.

Use a solution of lead nitrate or lead acetate.

1. **HCl** and soluble chlorides ppt. white crystalline lead chloride, $PbCl_2$, slightly soluble in cold water, much more so in hot. On cooling the hot solution it is pptd. again as crystalline needles.

2. **H_2S** ppts. black lead sulphide, PbS, insoluble in very dilute acids and in alkalis. From hydrochloric acid solutions the ppt. is at first reddish, [PbS, $PbCl_2$], which is turned black by more hydrogen sulphide (*cf.* mercuric salts). The pptn. is incomplete if the solution is strongly acid. PbS is soluble in hot dilute nitric acid, and is partly converted to lead sulphate if excess of the acid is used.

3. **KOH** ppts. white lead hydroxide, $Pb(OH)_2$, soluble in excess of the reagent to form potassium plumbite $Pb(OK)_2$.

4. **NH_4OH** also ppts. the hydroxide, *insoluble* in the reagent.

5. **K_2CrO_4** ppts. yellow lead chromate, $PbCrO_4$, insoluble in acetic, soluble in nitric acid. By the action of hot dilute alkalis it is converted in a red basic salt (p. 29).

6. **$K_2Cr_2O_7$** also ppts. $PbCrO_4$. If lead nitrate is used the reaction is

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2KNO_3 + 2HNO_3 + 2PbCrO_4,$$

and pptn. is therefore incomplete owing to the solubility of the chromate in nitric acid. The reaction becomes complete if excess of sodium acetate is added, whereby the nitric acid is replaced by acetic.

7. **KI** ppts. yellow lead iodide, PbI_2, soluble in *much* hot water to a *colourless* solution. On cooling this slowly the iodide is deposited in fine golden scales.

8. **H_2SO_4** ppts. white lead sulphate, $PbSO_4$, somewhat soluble in dilute nitric acid, completely in hot strong hydrochloric. It is much less soluble in presence of excess of *dilute* sulphuric acid, and completely insoluble in the presence of alcohol.

9. **Na_2HPO_4** ppts. white lead phosphate, insoluble in acetic acid.

10. **Na_2CO_3** ppts. basic lead carbonate. The *normal* carbonate is formed by using **$NaHCO_3$**.

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MERCURY(OUS) Hg = 200·0.

The two oxides, Hg_2O and HgO both give rise to salts, those of the former only giving a ppt. with hydrochloric acid. Mercury compounds are completely volatile on being heated strongly, unless the acid is non-volatile, in which case this, or a decomposition product, is left. (See mercurous chromate.) Nitric acid is the proper solvent for mercury. Hot strong nitric acid yields mercuric nitrate, cold dilute acid yields mercurous nitrate, especially if the mercury is kept in excess.

$$\text{Strong,}\quad 3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O.$$
$$\text{Dilute,}\quad 6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 2NO + 4H_2O.$$

Dry Tests.

All mercury compounds yield mercury when heated with sodium carbonate or lime.

Mercurous chloride sublimes, yielding a slightly grey sublimate, owing to the decomposition $Hg_2Cl_2 = Hg + HgCl_2$ taking place to a slight extent.

Mercurous nitrate, carefully heated, yields mercur*ic* oxide. (See preparation of HgO.)

Wet Tests.

Use a solution of mercurous nitrate in water with the least possible amount of dilute nitric acid to prevent the formation of a basic salt.

1. **HCl** ppts. calomel, Hg_2Cl_2, soluble in aqua regia or hot strong nitric acid, being oxidised to mercuric chloride. Hot strong sulphuric acid converts it to mercur*ic* sulphate, with difficulty.

$$Hg_2Cl_2 + 3H_2SO_4 = 2H_2O + 2HCl + SO_2 + 2HgSO_4.$$

Mercurous chloride is blackened by ammonia, forming mercuric amine chloride and mercury.

$$Hg_2Cl_2 + 2NH3 = NH_4Cl + Hg\begin{cases} NH_2 \\ Cl \end{cases} + Hg.$$

2. **KOH** ppts. black Hg_2O.
3. **NH_4OH** ppts. (from the nitrate) a black compound

$$O\begin{cases} Hg—NH_2 \\ Hg—NO_3 \end{cases} + 2Hg,$$

which on boiling with dilute HCl dissolves, leaving the mercury.

4. **H_2S** ppts. black mercur*ic* sulphide and mercury.

$$Hg_2(NO_3)_2 + H_2S = HgS + Hg + 2HNO_3.$$

5. **K_2CrO_4** ppts. a brown basic chromate, which on boiling changes to fiery red normal chromate.

$$3K_2CrO_4 + 4Hg_2(NO_3)_2 + H_2O = 6KNO_3 + 2HNO_3 + 3Hg_2CrO_4,\ Hg_2O,$$
$$3Hg_2CrO_4,\ Hg_2O + 2HNO_3 = 3Hg_2CrO_4 + H_2O + Hg_2(NO_3)_2.$$

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6. **KI** ppts. green Hg_2I_2, soluble in excess with separation of mercury.

$$Hg_2I_2 + 2KI = K_2HgI_4 + Hg.$$

7. **$SnCl_2$** ppts. grey metallic mercury.

$$Hg_2(NO_3)_2 + SnCl_2 + 2HCl = 2HNO_3 + SnCl_4 + 2Hg.$$

8. **Copper(foil)** ppts. mercury as a grey deposit on the copper. When rubbed it becomes bright.

GROUP II.

Group reagent H_2S in presence of dilute HCl.

MERCURY(IC) LEAD, COPPER, BISMUTH, CADMIUM (THALLIUM). SULPHIDES INSOLUBLE IN AMMONIUM SULPHIDE. (GROUP II. A.)

ARSENIC, ANTIMONY, TIN (GOLD, PLATINUM, VANADIUM, MOLYBDENUM, TUNGSTEN). SULPHIDES SOLUBLE IN AMMONIUM SULPHIDE. (GROUP II. B.)

MERCURY(IC).

DRY TESTS.

Mercuric salts of volatile acids are completely volatile when heated, with or without decomposition. Those containing oxygen decompose, so does the cyanide. Mercuric sulphide gives a black sublimate; mercuric iodide gives a yellow sublimate, which slowly returns to the red form; it turns at once when rubbed.

WET TESTS.

Use a solution of mercuric chloride, $HgCl_2$, in water, or of mercuric nitrate in water with the minimum of nitric acid.

Mercuric nitrate and sulphate are, like the mercurous salts, partly hydrolysed by water, giving basic insoluble salts. Mercuric cyanide, owing to its solution being practically non-ionised, gives reaction 1 only.

1. **H_2S** ppts. black HgS from acid solutions. The pptn. is very characteristic; white at first, it turns yellow, brown, and finally black. The white ppt. is $Hg_3S_2Cl_2$ (*i.e.* 2HgS, $HgCl_2$) which with more hydrogen sulphide is converted into HgS.

Mercuric sulphide is insoluble in boiling dilute acid. Hot strong nitric acid converts it into white $Hg_3S_2(NO_3)_2$. The correct solvent is aqua regia, which converts it into the chloride with separation of sulphur. Alkalis do not act on mercuric sulphide, nor does ammonium sulphide, but sodium (or potassium) sulphide readily dissolves it.

$$HgS + K_2S = Hg(SK)_2,$$

which is hydrolysed by water. Under suitable conditions the *red* variety is thus pptd. (See preparation.)

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2. **KOH** ppts. *yellow* amorphous oxide, HgO. The hydroxide is unknown.

3. **NH_4OH** produces a white ppt.

$$HgCl + 2NH_3 = NH4Cl + Hg\begin{cases} NH_2 \\ Cl \end{cases}$$

the so-called "white ppt." of medicine. From the nitrate an oxyamido compound is formed.

$$2Hg(NO_3)_2 + 4NH_3 + H_2O = 3NH_4NO_3 + O\begin{cases} Hg—NH_2 \\ Hg—NO_3. \end{cases}$$

4. **KI** ppts. red HgI_2 (yellow at first, quickly turning red), which is soluble in excess of potassium iodide or mercuric chloride.

5. **Na_2CO_3** ppts. a basic carbonate $3HgO . HgCO_3$.

The same ppt. is formed by $NaHCO_3$ with mercuric nitrate, but not from the chloride.

6. **K_2CrO_4** ppts. yellow $HgCrO_4$. **Dichromates** produce a ppt. with the nitrate, but not with the chloride.

7. **$SnCl_2$** ppts. first white mercurous chloride, which is further reduced by more stannous chloride, especially on warming, to grey metallic mercury.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

If the solution is decanted and the ppt. warmed with hydrochloric acid, the mercury forms globules.

Many other reducing agents cause the pptn. of metallic mercury.

8. **Copper** ppts. metallic mercury from solution in the same manner as with mercurous salts.

The reactions of **lead** have already been studied. Owing to the slight solubility of lead chloride, lead sulphide is always pptd. in this group. The same remark applies to **thallium.**

COPPER, Cu = 63·57.

The two oxides of copper, Cu_2O and CuO, both give rise to salts. Cuprous salts are insoluble, however, and are oxidised to cupric salts to get them into solution, and hence copper does not appear in Group I.

Dry Tests.

These are common to both cuprous and cupric salts.

On charcoal in the reducing flame, especially with fusion mixture, or on the charcoal stick, scales of copper are obtained. These do not form a bead, owing to the high melting point of copper.

The borax-bead is greenish-blue. In the reducing flame (especially with a trace of stannous chloride) a transparent red bead is obtained.

Many copper salts colour the flame green. Copper halides impart a magnificent peacock-green colour to the flame.

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Wet Tests.

Cuprous Salts.

A solution of cuprous chloride in strong hydrochloric acid is used.

1. **H_2S** ppts. black Cu_2S, soluble in hot dilute nitric acid.

2. **KOH** ppts. orange-yellow cuprous hydroxide, $Cu_2(OH)_2$, which is dehydrated on boiling, becoming red Cu_2O.

Cupric Salts.

Use a solution of copper sulphate.

1. **H_2S** ppts. black CuS. In neutral or slightly acid solutions this is colloidal and cannot be filtered. From more strongly acid solutions a gel ppt. is obtained. It is soluble in hot dilute nitric acid, appreciably soluble in *yellow* ammonium sulphide, insoluble in potassium (or sodium) sulphide.

2. **KOH** ppts. blue gelatinous $Cu(OH)_2$, turning black on boiling, owing to dehydration.

3. **NH_4OH** ppts. at first a green basic sulphate, $Cu_2(OH)_2SO_4$, soluble in excess, forming a fine blue solution of aquo-tetrammine copper sulphate. (See preparation.)

$$2CuSO_4 + 2NH_4OH = (NH_4)_2SO_4 + Cu_2(OH)_2SO_4.$$

$$Cu_2(OH)_2SO_4 + (NH_4)_2SO_4 + 6NH_3 = 2Cu(NH_3)_4SO_4 . H_2O.$$

4. **KCN** ppts. $Cu(CN)_2$, which becomes $Cu_2(CN)_2$ by loss of cyanogen. This is soluble in more potassium cyanide to form the cupro-cyanide.

$$CuSO_4 + 2KCN = K_2SO_4 + Cu(CN)_2.$$

$$2Cu(CN)_2 = C_2N_2 + Cu_2(CN)_2.$$

$$Cu_2(CN)_2 + 6KCN = 2K_3[Cu(CN)_4].$$

A similar compound is formed when potassium cyanide in excess is added to the blue ammoniacal solution of 3. If *excess* of cyanide is added, the cupric ions are suppressed, and then hydrogen sulphide causes no ppt. (Difference from Cadmium.)

5. **KCNS** ppts. black sulphocyanate, $Cu(CNS)_2$, gradually turning to white $Cu_2(CNS)_2$, especially on addition of sulphurous acid.

$$2Cu(CNS)_2 + H_2O + H_2SO_3 = H_2SO_4 + 2HCNS + Cu_2(CNS)_2.$$

6. **$K_4Fe(CN)_6$** ppts. brown gelatinous $Cu_2Fe(CN)_6$, insoluble in dilute acids, decomposed by alkalis, yielding blue $Cu(OH)_2$. (*Cf.* Uranium.)

BISMUTH, Bi = 208·0.

Bismuth oxides are Bi_2O_3, Bi_2O_4, and Bi_2O_5. The first-named only is basic (for further properties see preparations), and all bismuth salts correspond to it.

Dry Tests.

On charcoal in the reducing flame, bismuth salts yield a brittle metallic bead and a yellow incrustation of oxide. Fusion mixture should be added if any difficulty is experienced in getting a bead. The metal is soluble in nitric acid.

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On an asbestos thread in the upper reducing flame bismuth compounds are reduced to metal, which burns to oxide in the upper oxidising flame, forming an almost invisible "flash" on a cold porcelain dish held *above* the flame (see p. 79). On treatment with hydriodic acid, a scarlet deposit is formed.

$$Bi_2O_3 + 8HI = 3H_2O + 2HBiI_4,$$

which disappears when breathed upon and reappears when dried. By blowing ammonia on to it, it becomes a fine salmon red.

$$HBiI_4 + NH_3 = NH_4BiI_4,$$

also becoming invisible when breathed upon.

Von Kobell's reaction.—Mix a bismuth compound with potassium iodide and sulphur, and heat on charcoal. A magnificent red incrustation of BiSI is formed.

Wet Tests.

Use a solution of bismuth nitrate with addition of a little acid.

1. **H_2S** ppts. dark brown Bi_2S_3, insoluble in dilute acids (except nitric), and in alkali sulphides.

2. **KOH** and **NH_4OH** ppt. white $Bi(OH)_3$, insoluble in excess of either reagent.

3. **$K_2Cr_2O_7$** ppts. yellow basic (bismuthyl) dichromate

$$K_2Cr_2O_7 + 2BiCl_3 + 2H_2O = 2KCl + (BiO)_2Cr_2O_7,$$

soluble in mineral acids.

4. **KI** ppts. black BiI_3, soluble in excess to an orange liquid

$$BiI_3 + KI \rightleftarrows KBiI_4$$

which is decomposed again by not too much water. By boiling with water a red basic iodide BiOI is formed.

5. **Sodium stannite, $Sn(ONa)_2$** (produced by adding caustic alkali to a few drops of stannous chloride till the ppt. redissolves, and then diluting with water) ppts. black metallic bismuth.

$$SnCl_2 + 2KOH = Sn(OH)_2 + 2KCl$$
$$Sn(OH)_2 + 2KOH = Sn(OK)_2 + 2H_2O$$
$$2BiCl_3 + 6KOH = 6KCl + 2Bi(OH)_3$$
$$2Bi(OH)_3 + 3Sn(OK)_2 = \underset{\text{(stannate)}}{3SnO(OK)_2} + 2Bi + 3H_2O.$$

The test requires both care and experience. Carry out as indicated, avoid a large excess of alkali and do not heat.

6. **Water** causes hydrolysis of bismuth salts, giving a white ppt. of a basic salt, the exact composition of which depends on dilution and temperature.

CADMIUM, Cd = 112·40.

There are two oxides, Cd_2O (?) white, and CdO brown. The salts correspond to the latter oxide.

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Dry Tests.

On charcoal in the reducing flame a variously coloured residue is obtained, with a brown incrustation. When " flashed " on the asbestos thread, the basin being held above the flame, a brown film of the oxide is obtained. It is edged with the white (invisible) sub-oxide which is a reducing agent. If a strip of filter paper moistened with silver nitrate solution be drawn across the deposit a blue-black deposit of metallic silver is obtained.

In this manner the ppt. of sulphide obtained in the group may be confirmed. The sulphide should first be roasted to the oxide in the upper oxidising flame before being reduced.

Wet Tests.

1. **H_2S** ppts. yellow CdS from acid solutions. The sulphide is insoluble in cold dilute hydrochloric or sulphuric acid, but readily soluble in warm dilute nitric or sulphuric and strong hydrochloric acids. It is insoluble in alkaline sulphides.

CdS often appears as a colloidal ppt. impossible to filter, if the pptn. is made from hydrochloric acid solution. It is advantageous to employ sulphuric acid if possible.

2. **KOH** ppts. white $Cd(OH)_2$, insoluble in excess.

3. **NH_4OH** gives the same ppt. soluble in excess of the reagent (*cf.* zinc etc.), the complex cadmium ammonia compound is hydrolysed, however, by boiling with much water.

4. **KCN** ppts. white $Cd(CN)_2$ soluble in excess of the reagent, forming $K_2Cd(CN)_4$. Of the above reagents, hydrogen sulphide alone causes a ppt. from this solution (separation from copper).

ARSENIC, As = 75·0.

The oxides of arsenic, As_4O_6 and As_2O_5 almost always act as acid anhydrides. The chloride $AsCl_3$ is more or less completely decomposed by water, an aqueous solution of it (and a solution of As_4O_6 in dilute hydrochloric acid) containing the arsenic as arsenious acid

$$AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl.$$

Dry Tests.

Common to both arsenious and arsenic compounds.

The oxides, etc. are completely volatile on charcoal, being reduced to the element, which burns again, giving off a characteristic garlic smell. *All* arsenic compounds give this odour when heated on charcoal with fusion mixture. (Poison!)

Arsenic compounds reducible to the element give either a metallic or an oxide " flash " according to the position of the porcelain basin. The metallic film is brownish black, soluble in hypochlorite solution (difference from antimony)

$$2As + 5NaOCl + 3H_2O = 5NaCl + 2H_3AsO_4.$$

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The oxide film is white. Ammonium sulphide vapour turns it yellow (As_2S_3).

N.B.—Arsenic sulphides must be roasted carefully to the oxide before being "flashed."

Arsenic compounds colour the bunsen flame steel-blue, due to the reduced arsenic burning again. Heated with charcoal in a dry tube, the oxides yield a mirror of metallic arsenic. To carry out the test, a match stick is thoroughly charred (heated under sand) and introduced into a tube of hard glass drawn out as shown. A small quantity of arsenious oxide is placed at the bottom,

FIG. 29.

the charcoal is made red hot, and the arsenic then heated. A metallic mirror is obtained. If this is heated it sublimes higher up the tube as the trioxide, in characteristic glistening octahedra, which are easily seen under a lens.

WET TESTS.

Arsenious Acid.

Use a solution of arsenious oxide in dilute hydrochloric acid.

1. **H_2S** ppts. from acid solution yellow As_2S_3, insoluble in acids (even strong hydrochloric acid) but soluble in strong nitric acid, forming arsenic and sulphuric acids (oxidation). It is soluble in alkalis, ammonium carbonate and alkali sulphides, forming arsenites, thio-arsenites or both. The reactions may be simply formulated :

(1) $$6KOH + As_2S_3 = 3H_2O + K_3AsO_3 + K_3AsS_3$$

(2) $$3(NH_4)_2CO_3 + As_2S_3 = 3CO_2 + (NH_4)_3AsO_3 + (NH_4)_3AsS_3$$

(3) $$3(NH_4)_2S + As_2S_3 = 2(NH_4)_2AsS_3.$$

On acidifying these solutions As_2S_3 is repptd.

Yellow ammonium sulphide (containing sulphur in excess) oxidises it to ammonium thio-arsen*ate*

$$3(NH_4)_2S + As_2S_3 + 2S = 2(NH_4)_3AsS_4.$$

As_2S_3 is not pptd. from an *aqueous* solution of As_2O_3, as it remains in the colloidal state (yellow liquid). It is coagulated by the addition of dilute hydrochloric acid. (See p. 73.)

2. **$AgNO_3$** in *neutral* arsenite solution (use aqueous sodium arsenite) produces yellow silver arsenite, soluble in nitric acid and ammonia.

3. **$CuSO_4$** in *neutral* arsenite solutions ppts. green copper arsenite (Scheele's green). $CuHAsO_3$.

Arsenic Acid.

Use a solution of an alkali arsenate.

1. **H_2S**, in the presence of *much strong hydrochloric acid, in the cold,* ppts. the yellow penta-sulphide, As_2S_5; $2H_3AsO_4 + 5H_2S = 8H_2O + As_2S_5$.

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If hot, a mixture of tri- and penta-sulphides is formed.

In a cold dilute hydrochloric acid solution such as is obtained for analysis, hydrogen sulphide ppts. *very slowly* a mixture of sulphur and the tri-sulphide thus:

First $H_3AsO_4 + H_2S = H_2O + H_3AsO_3 + S$

and then $2H_3AsO_3 + 3H_2S = 6H_2O + As_2S_3$.

Various other reducing agents, *e.g.* sulphurous acid, reduce arsen*ic* to arsenio*us* acid. It is advantageous to perform this reduction, boiling off excess of sulphur dioxide, before passing hydrogen sulphide.

Arsenic penta-sulphide is soluble in alkalis, alkali sulphides and ammonium carbonate, forming thio- and partly thio-arsenates

$$As_2S_5 + 6KOH = 3H_2O + K_3AsS_4 + K_3AsSO_3$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4.$$

These solutions yield arsenic penta-sulphide again on acidification.

2. **$AgNO_3$** in neutral solutions ppts. brick-red silver arsenate, Ag_3AsO_4, soluble in nitric acid and in ammonia (difference from arsenite).

3. **Magnesium mixture** $[(NH_4)_2MgCl_4 + NH_4OH]$ ppts. from ammoniacal solutions white crystalline magnesium ammonium arsenate,

$$MgNH_4AsO_4,\ 6H_2O,$$

which is in every way analogous to the corresponding phosphate (difference from arsenite).

4. **Ammonium molybdate** in excess ppts. from a hot *nitric* acid solution, yellow crystalline ammonium arsenomolybdate, $(NH_4)_3AsO_4 + 12MoO_3$, soluble in alkalis and ammonia (difference from arsenite).

N.B. By boiling arsenites with much strong nitric acid, the yellow ppt. may be produced slowly, owing to oxidation to arsenates.

5. **$CuSO_4$** ppts. pale greenish-blue $CuHAsO_4$ (difference from arsenite).

Wet Tests Common to Both.

1. **Reinsch's Test.**—A strip of copper foil warmed with arsenious or arsenic acid is covered with a deposit of metallic arsenic.

2. **Nascent Hydrogen** (acid) reduces all arsenic compounds to the hydride, AsH_3. On this fact depend

(*a*) **Marsh's Test.**—*Pure* zinc and *pure* dilute sulphuric acid are placed in a small flask fitted as shown. A few drops of platinic chloride are added to facilitate the evolution of hydrogen (which is very slow from *pure* reagents).

When all air is swept out of the apparatus, the gas is lighted at the jet. On adding to the flask a few drops of a solution of any arsenic compound, arsine is produced. It is detected by

(1) Heating the tube strongly, which decomposes the hydride, forming a mirror of metallic arsenic on the tube.

(2) The steel-blue colour imparted to the hydrogen flame.

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(3) Holding the lid of a porcelain crucible in the flame for a few seconds. A black stain of arsenic is obtained, soluble in hypochlorites (difference from antimony).

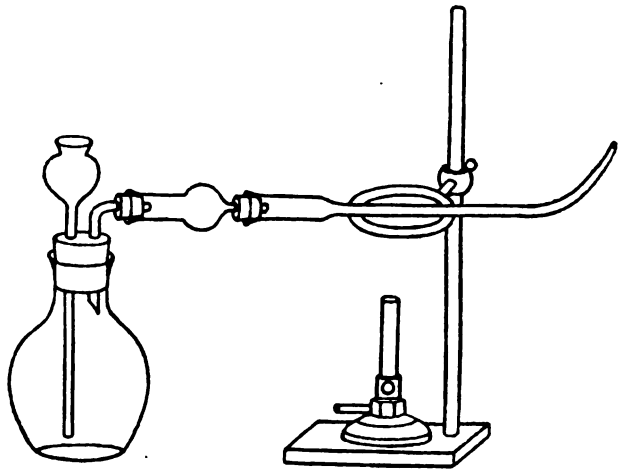

FIG. 30.

Marsh's test is exceedingly delicate, and it is usually necessary to perform a blank test with the reagents, which both contain arsenic unless specially purified.

Arsine is exceedingly poisonous.

(*b*) **Gutzeit's test.**—Arsine colours a crystal of silver nitrate yellow. On moistening it, the colour changes to black.

1. $$6AgNO_3 + AsH_3 = AsAg_3 . \underbrace{3AgNO_3 + 3HNO_3}_{\text{yellow}}$$

2. $$AsAg_3 . 3AgNO_3 + 3H_2O = H_3AsO_3 + 3HNO_3 + 6Ag.$$

The test is carried out either by leading arsine (produced as in Marsh's test) through silver nitrate *solution*, when the black ppt. of silver is produced *at once*, or as shown in Fig. 31 (Eidenbenz's modification of Gutzeit's test), where the yellow colour is seen first. The figure explains itself.

N.B.—To detect arsenic (Scheele's green) in coloured matter, such as wall-paper, the substance is extracted with dilute hydrochloric acid and the solution submitted to any of the above tests.

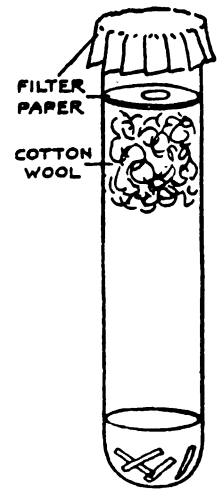

FIG. 31.

ANTIMONY, Sb = 120·2.

There are three oxides.

Sb_2O_3, basic and acidic; Sb_2O_5, acidic; Sb_2O_4, indifferent, probably basic antimony met-antimonate $(SbO)SbO_3$.

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Dry Tests.

Common to both types.

Heated on charcoal, especially with fusion mixture, a brittle bead is obtained, together with a white incrustation (difference from bismuth).

The oxides may be "flashed" and a metallic or an oxide film produced at will (sulphides should first be roasted in upper oxidising flame). The metallic film is insoluble in hypochlorite solution (difference from arsenic). The oxide film is coloured orange by ammonium sulphide vapour.

Antimony compounds colour the flame a steel-white colour (reduced metal burning). The correct solvent for antimony is aqua regia. Nitric acid yields Sb_2O_5, a white insoluble powder.

A. Antimonious Compounds.

Use a solution of Sb_2O_3 in dilute hydrochloric acid.

1. **H_2S** ppts. orange-red trisulphide Sb_2S_3 from dilute acid solution; readily soluble in strong hydrochloric acid and hence incompletely pptd. unless the acid is *very* dilute. Sb_2S_3 is soluble in alkaline sulphides and in alkalis, including lime-water.

2. **Water** ppts. a basic salt, changed to the hydroxide by much hot water. (See preparations, basic salts). These are all soluble in alkali tartrate solution, forming tartar emetic (p. 32).

3. **KOH, NH_4OH, and alkali carbonates** ppt. the hydrated oxide, soluble in excess of alkali.

4. **Zinc** ppts. metallic antimony. A Zn-Pt couple (piece of zinc resting on platinum foil) in an antimony solution in hydrochloric acid ppts. the antimony as a velvety stain on the platinum, insoluble in hydrochloric acid.

B. Antimonic Compounds.

Use a solution of potassium antimonate $KSbO_3$.

1. **H_2S** ppts. from moderately acid solution orange-red Sb_2S_5, soluble in strong hydrochloric acid

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + 2S$$

and in alkali sulphides and alkalis, but not in ammonium carbonate (separation from arsenic), forming similar compounds to those of arsenic.

2. **H_2O** hydrolyses the antimonates, ppting. white antimonic acid.

N.B. The antimonates corresponding to the various phosphates are not all known. The commonest are the metantimonate $KSbO_3$, and pyroantimonate, $K_4Sb_2O_7$, hydrolysed to $K_2H_2Sb_2O_7$, soluble in warm water. This is a reagent for sodium, the sodium salt being less soluble. The reagent does not keep in solution, however, as it readily adds on water.

$$K_2H_2Sb_2O_7 + H_2O = 2KH_2SbO_4 \text{ (ortho)}.$$

Reactions common to both types.

Nascent Hydrogen reduces all antimony compounds to stibine, SbH_3, and consequently Marsh's test, with antimony compounds, gives results very

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similar to those obtained with arsenic. The distinction is that the antimony deposit obtained on the crucible lid is insoluble in hypochlorite.

Gutzeit's Test gives results similar in appearance to those obtained with arsenic. The black ppt. with silver nitrate solution, however, is silver antimonide,

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3,$$

whereas that obtained with arsine is metallic silver.

Zinc-Platinum couple. If a piece of pure zinc in contact with a piece of platinum foil be placed in a hydrochloric acid solution of an antimony compound, the antimony is deposited on the platinum as a black velvety stain (separation from tin.)

TIN, Sn = 119·0.

Tin forms two oxides, SnO, black, readily oxidised and chiefly basic, and SnO_2, chiefly acidic. The most common salts are stannous chloride and sulphate, $SnCl_2$ and $SnSO_4$, and stannic chloride, $SnCl_4$, $4H_2O$. The latter possesses some of the properties of a non-metallic (acid) chloride, but yields double salts, "pink salt" $(NH_4)_2SnCl_6$, ammonium stannichloride, being the best known.

The correct solvent for tin is hot strong hydrochloric acid. Nitric acid converts it into metastannic acid, H_2SnO_3, a white insoluble powder.

Dry Tests.

Common to stannous and stannic compounds.

On charcoal, with fusion mixture, a bead of metallic tin is obtained; it is, however, somewhat difficult to get a bead of any size. If potassium cyanide be mixed with the fusion mixture, the bead is far more readily formed. It is also readily obtained with the charcoal stick. The bead is malleable and does *not* form a clear solution with nitric acid (see above; difference from silver).

Wet Tests.

Stannous Compounds.

Use a solution of stannous chloride.

1. **H_2S** ppts. dark brown stannous sulphide, SnS, soluble in much hot hydrochloric acid, and in *yellow* ammonium sulphide and sodium '*per*'-sulphide, forming sulphostann*ates*.

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

SnS_2 is pptd from this solution on acidification.

2. **KOH** ppts. white stannous hydroxide, $Sn(OH)_2$, soluble in excess forming potassium stannite.

$$Sn(OH)_2 + 2KOH = Sn(OK)_2 + 2H_2O.$$

On the strongly alkaline solution being warmed, a black ppt. of SnO is formed.

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3. **$HgCl_2$** is reduced to white insoluble Hg_2Cl_2, which in excess of the stannous salt is further reduced to grey metallic mercury.

4. **$AuCl_3$** is reduced to finely divided (colloidal) metallic gold (Purple of Cassius)

$$2AuCl_3 + 3SnCl_2 = 3SnCl_4 + 2Au.$$

5. **H_2O** causes the pptn. of basic salts. For this reason a solution of stannous chloride should contain a little dilute hydrochloric acid, and some tin to prevent the formation of stannic chloride.

Stannic Compounds.

There are two classes of these, known as α-stannic and β-stannic compounds. The former are the ordinary ones derived from stannic hydroxide pptd. by adding potash to stannic chloride solution. Dried in a desiccator this ppt. has the composition $SnO(OH)_2$ or H_2SnO_3. It is soluble in both acids and alkalis. The stannates are derived from the above hydroxide and are therefore *meta*-stannates.

α-Stannic Compounds.

Use a solution of ammonium stannic chloride in water.

1. **H_2S** ppts. yellow SnS_2, soluble in much hydrochloric acid, also in alkali sulphide, forming thio-stannate, from which acids reppt. SnS_2 (see also "mosaic gold," p. 164).

2. **KOH** ppts. white $Sn(OH)_4$, soluble in excess of the reagent (see above).

3. **NH_4OH** produces the same ppt. as KOH; tartaric acid prevents its formation (difference from β-stannic acid).

β-Stannic Compounds.

The acid H_2SnO_3 formed by the action of nitric acid on tin has the same empirical formula as α-stannic acid, but differs from it in many respects.

1. It is not so readily soluble in dilute mineral acids. With hydrochloric it forms a stannyl chloride $Sn_5O_5(OH)_8Cl_2$ (Engel, *Chem. Zeit.*, 1897, p. 309), which is pptd. on the addition of strong hydrochloric acid as a less basic salt.

2. An aqueous solution of this stannic chloride is boiled. β-stannic acid is repptd.

3. **H_2S** ppts. from *dilute* acid solutions yellow SnS_2.

4. **H_2SO_4** ppts. from stannyl chloride solution white stannyl sulphate (difference from α-chloride).

5. **KOH** ppts. β-stannic acid, insoluble in *strong* potash, but more easily soluble in dilute potash, forming a β-stannate, $Sn_5O_5(OK)_2(OH)_8$.

6. **NH_4OH** ppts. β-stannic acid, insoluble in tartaric acid (difference from α-stannic chloride).

Generally speaking, the dilute aqueous α-compounds are changed, especially by boiling, into the β-compounds. The reverse change takes place by treating the β-compound with *strong* alkali or hydrochloric acid (former for salts, latter for acid itself).

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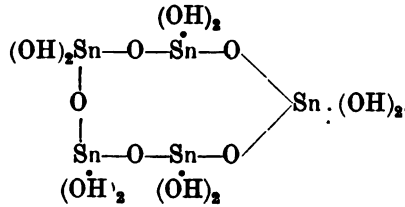
It may be said that β-stannic acid is probably a polymer of α-stannic having the formula $(H_2SnO_3)_5$ or



The deduction of the various reactions may be left to the student.

Reactions common to both -ous and -ic compounds.

7. **Metallic Zinc** ppts. tin from all tin solutions, as a spongy mass on the zinc. It is easily soluble in hydrochloric acid, but a Zn-Pt couple (see antimony) ppts. it on the zinc (and partly on the platinum) in spite of the presence of hydrochloric acid (electrolysis).

GOLD, Au = 197·2.

Oxides.—Aurous oxide, Au_2O, Auric oxide, Au_2O_3. Both basic. Aurous salts seldom met with. Aurous chloride is insoluble in water. Auric salts mostly yellow in colour and readily soluble in water. Gold oxides and salts are all unstable, and ignition decomposes them completely, leaving a residue of gold.

Dry Tests.

All gold compounds on charcoal with fusion mixture yield a bead of metallic gold.

Wet Tests (Auric only).

Use a solution of hydrochlorauric acid, $HAuCl_4$.

1. **H_2S** ppts. black Au_2S_2, insoluble in dilute mineral acids, somewhat soluble in yellow ammonium sulphide; it is better to use K_2S_2.

$$Au_2S_2 + K_2S_2 = 2KAuS_2.$$

The pptn. by H_2S should be done in a *cold* solution, as in hot solutions gold is pptd. owing to the reducing action of the H_2S.

$$8AuCl_3 + 3H_2S + 12H_2O = 24HCl + 2H_2SO_4 + 8Au.$$

2. **KOH** ppts. reddish brown $Au(OH)_3$, soluble in excess to form $KAuO_3$. Very dilute alkali should be used, or owing to the dilute gold solution the ppt. may be immediately redissolved and missed.

3. **NH_4OH** ppts. yellow "fulminating gold," $Au(NH_3)_2(OH)_2$, which explodes violently when dried and heated or struck.

4. **Reducing agents** ppt. metallic gold, the appearance of which differs according to the reagent used. The most characteristic reaction is with **Stannous chloride**, which ppts. the gold as a purple ppt. (Purple of Cassius) turning brown very quickly. Much acid prevents the pptn.

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H_2O_2 reduces gold from alkaline solutions as a brown finely divided substance.

Oxalic acid ppts. gold completely on warming (separation from platinum).

$$2AuCl_3 + 3H_2C_2O_4 = 6HCl + 6CO_2 + 2Au.$$

Ferrous sulphate reacts similarly, as also does **sulphurous acid**.

PLATINUM, Pt = 194·9.

Oxides PtO and PtO_2. Both basic. The solvent for Pt is aqua regia. If alloyed with silver it will dissolve in nitric acid (difference from gold). The solution in aqua regia yields chlorplatinic acid, H_2PtCl_6, on evaporation. Excess of chlorine is necessary to prevent the formation of chlorplatinous acid, H_2PtCl_4.

Dry Tests.

Heated with fusion mixture on charcoal, a grey spongy metallic mass is obtained.

Wet Tests.

Use a solution of H_2PtCl_6.

1. **H_2S** ppts. black PtS_2 slowly when cold, quickly on warming, soluble in alkali polysulphide.
2. **NaOH** (*not* **KOH**) ppts. black $Pt(OH)_4$.
3. **KCl or NH_4Cl** from not too dilute solutions ppt. yellow crystalline K or $(NH_4)_2PtCl_6$.
4. **Reducing agents** do not reduce platinum salts to metal so readily as they do gold salts. Thus:

Oxalic acid has no action.

$FeSO_4$ only in neutral solutions on warming.

$SnCl_2$ reduces them to H_2PtCl_4 only, when warmed.

Glycerine and NaOH ppt. the metal as a black powder.

$$C_3H_5(OH)_3 + 3Na_2PtCl_6 + 16NaOH$$
$$= 3Pt + Na_2C_2O_4 + Na_2CO_3 + 12H_2O + 18NaCl.$$

Formic acid ppts. the metal from neutral boiling solutions as a black powder.

$$2HCO_2H + H_2PtCl_6 = 6HCl + 2CO_2 + Pt.$$

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GROUP III.

Reagent.—Ammonium sulphide in presence of ammonium chloride and ammonia.

ALUMINIUM, CHROMIUM, IRON, TITANIUM, URANIUM (PPTD. AS HYDROXIDES), NICKEL, COBALT, MANGANESE, ZINC (PPTD. AS SULPHIDES).

The rare earths are also pptd. as hydroxides in this group, but it is usual to remove the bulk of them as oxalates after Group II. (*See p.* 183.)

ALUMINIUM, Al = 27·1.

The metal is practically insoluble in nitric acid. Correct solvent, strong HCl.

Oxide, Al_2O_3, basic (Acidic to potash and soda). Insoluble in acids after ignition when correct solvent is molten $KHSO_4$.

DRY TESTS.

On charcoal before the blowpipe, all aluminium salts except those of non-volatile acids (such as phosphoric and silicic) leave a white infusible residue of alumina, Al_2O_3, incandescent when hot. This, when moistened with cobalt nitrate and heated strongly, forms a blue mass, **Thénard's blue.** Aluminium salts are similarly decomposed by ignition in air.

DRY TESTS.

Use a solution of common alum, $Al_2(SO_4)_3,K_2SO_4,24H_2O$.

1. **NH_4OH** ppts. almost colourless gelatinous $Al(OH)_3$, which is only completely insoluble in the presence of ammonium salts. In their absence it forms a hydrosol, impossible to filter. $Al(OH)_3$ is soluble in dilute acids when freshly pptd., but becomes more insoluble on standing, due to partial dehydration.

2. **KOH** ppts. $Al(OH)_3$, soluble in excess, forming potassium aluminate, $Al(OK)_3$. This is not readily hydrolysed by boiling, but by adding ammonium salts it decomposed completely, owing to the immediate hydrolysis of ammonium aluminate

$$Al(OK)_3 + 3NH_4Cl = 3KCl + Al(ONH_4)_3$$

and then

$$Al(ONH_4)_3 + 3H_2O = 3NH_4OH + Al(OH)_3.$$

When a solution of an aluminate is acidified a ppt. of $Al(OH)_3$ is first formed, $Al(OK)_3 + 3HCl = Al(OH)_3 + 3KCl$, which readily dissolves in more acid.

The presence of some organic acids, especially tartaric and citric, prevents the pptn. of aluminium hydroxide by the alkalis, owing to the formation of a "double" salt in which the aluminium is in the negative ion. Sugar and starch produce a similar effect. If these are present they must therefore be destroyed before coming to Group III.

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3. **$(NH_4)_2S$** ppts. $Al(OH)_3$ owing to the immediate hydrolysis of the sulphide by water.

4. **Alkali carbonates, $BaCO_3$ (suspended)**, etc., ppt. $Al(OH)_3$ owing to hydrolysis.

5. **Alkali acetates** produce no ppt. in cold solutions, but on boiling a basic acetate is produced by hydrolysis.

$$Al(C_2H_3O_2)_3 + 2H_2O \rightleftarrows Al(OH)_2(C_2H_3O_2) + 2C_2H_4O_2$$

(*cf.* iron and chromium).

6. **Na_2HPO_4** ppts. white gelatinous $AlPO_4$, insoluble in acetic acid, soluble in mineral acids. It is liable (in the cold) to assume a hydrosol form, which gelatinises when heated.

CHROMIUM, Cr = 52·1.

The metal is rendered "passive" by nitric acid, which therefore fails to dissolve it. Correct solvent, HCl.

Oxides.—$Cr(OH)_2$ (Anhydride unknown) Basic. Extremely unstable, rapidly absorbing oxygen to form chromic compounds. The acetate is the most stable salt known. Salts practically never met with unless specially prepared for absorption of oxygen in gas analysis.

Cr_2O_3 (green). Basic (acidic to potash and soda when in the hydrated form). Insoluble in acids or alkalis, after ignition.

CrO_3 (red, crystalline). Acid anhydride, soluble in water.

Dry Tests.

On charcoal before the blowpipe all chromium compounds leave a green residue of chromic oxide, Cr_2O_3, unless the acid is non-volatile, as phosphoric. $CrPO_4$ is itself green.

The borax bead is coloured emerald green by all chromium compounds, both in the oxidising and reducing flames.

Wet Tests.

I. Chromic Salts.

Use a solution of chrome alum.

1. **NH_4OH** ppt. green-grey or violet-grey (according to conditions) $Cr(OH)_3$ somewhat soluble in excess of ammonia, repptd. by boiling off the ammonia. Hence to ppt. $Cr(OH)_3$ completely avoid large excess of ammonia and boil. Cr_2O_3 is left when the hydrate is ignited. It is quite insoluble in acids. Correct solvent, molten $KHSO_4$ (*cf.* Aluminium).

2. **KOH** ppts. green-grey $Cr(OH)_3$ soluble in excess to form green $Cr(OK)_3$ potassium chromite, completely hydrolysed by diluting and boiling (difference from aluminium).

3. **Alkali carbonates and sulphides, $BaCO_3$**, etc. all ppt. $Cr(OH)_3$ as with aluminium.

4. **Na_2HPO_4** ppts. green $CrPO_4$ soluble in mineral acids and cold acetic acid, insoluble in hot acetic acid.

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5. **Alkali acetates** react as with aluminium, but on boiling the hydrolysis is incomplete unless excess of aluminium or ferric salts are present.

II. Chromates.

CrO_3 when neutralised by alkalis gives yellow chromates, *e.g.* K_2CrO_4, or orange dichromates, *e.g.* $K_2Cr_2O_7$. Bichromates, *e.g.* $KHCrO_4$, are unknown for $2KHCrO_4 = K_2Cr_2O_7 + H_2O$ even in solution.

When alkali is added to a dichromate solution the colour changes to yellow, owing to a chromate being formed.

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

When acid is added to a chromate solution the colour changes to orange, owing to the formation of a dichromate.

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O.$$

Chromic compounds are oxidised to chromates in alkaline solution (*i.e.* chromites) by hydrogen peroxide, chlorine, bromine, hypochlorites, etc., lead peroxide; in neutral solution by freshly pptd. manganese dioxide; or by halogens in presence of much sodium acetate; in acid solution only by potassium chlorate in presence of strong nitric acid.

In the dry way, oxidation is effected by fusion with alkali and an oxidising agent (see $K_2Cr_2O_7$ preparation, p. 61).

Equations :—

$$2Cr(OK)_3 + 4KOH + 3Cl_2 = 6KCl + H_2O + K_2CrO_4.$$

$$2CrCl_3 + 16Na(C_2H_3O_2) + 8H_2O + 3Cl_2 = 12NaCl + 16H(C_2H_3O_2) + 2Na_2CrO_4.$$

$$2CrCl_3 + 3MnO_2 + 2H_2O = 3MnCl_2 + 2H_2CrO_4.$$

Chromates and chromic acid are readily reduced in acid solutions by ferrous salts, sulphurous acid, hydrogen sulphide, alcohol, oxalic acid and hydriodic acid. Hot strong hydrochloric acid is also oxidised to chlorine. Hot strong sulphuric caused reduction with evolution of oxygen.

Reactions for chromic acid.

Use solution of potassium chromate or dichromate.

1. **Dilute H_2SO_4.**—Change of colour from yellow to orange in case of chromates; alkalis turn it back to yellow.

2. **Strong H_2SO_4.**—Orange red colour, often with separation of scarlet ppt. of trichromates or chromic acid. When heated oxygen is evolved and the solution slowly turns green.

3. **$AgNO_3$** ppts. crimson Ag_2CrO_4 from neutral solutions, soluble in acids and ammonia.

4. **$Pb(C_2H_3O_2)_2$** ppts. yellow $PbCrO_4$, soluble in mineral acids, insoluble in acetic.

5. **$BaCl_2$** ppts. lemon-yellow $BaCrO_4$, soluble in mineral acids, insoluble in acetic.

6. **$Hg_2(NO_3)_2$** ppts. brown basic mercurous chromate which on boiling forms fiery red normal chromate. (See under mercury for reactions.)

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7. **H_2O_2** and *free* chromic acid react to form a deep blue solution, probably perchromic acid, $H_2Cr_2O_8$, which is very unstable. The blue substance is, however, soluble in ether, in which it is more stable. To carry out the test, acidify the chromate solution with dilute sulphuric acid, add some ether, then a few drops of hydrogen peroxide and shake.

IRON, Fe = 55·9.

The correct solvent for the metal is hot dilute hydrochloric acid.

Oxides.—FeO basic, soluble in mineral acids, forming *ferrous* salts; Fe_2O_3 basic, soluble in dilute mineral acids (unless recently ignited or native, when hot strong hydrochloric acid is necessary) forming *ferric* salts; Fe_3O_4, soluble in hot strong hydrochloric acid, forming both ferrous and ferric salts. It is therefore a compound of the other two oxides.

Dry Tests.

On charcoal before the blowpipe, especially by the help of fusion mixture iron salts are reduced to black metallic iron, the grains of which can be picked out by a magnet (crush with water if fusion mixture has been used). The charcoal stick gives a similar reaction. The borax bead is coloured yellow in the oxidising flame (ferric), pale green in the reducing flame (ferrous). Some organic salts of iron, notably the oxalate, leave pyrophoric iron or ferrous oxide when heated strongly.

Wet Tests.

I. Ferrous Salts.

Use a fresh solution of ferrous sulphate in cold boiled water.

1. **NH_4OH** gives a ppt. of $Fe(OH)_2$. If absolutely pure this is white, but rapidly turns to a dirty green, then black and finally brown, owing to oxidation to ferric hydroxide. $Fe(OH)_2$ is soluble in ammonium chloride, forming a "double" salt with the iron in the complex negative ion. It is readily oxidised by the air, however, forming a messy ppt. of $Fe(OH)_3$. Owing to this it is quite impossible to filter off the ppt. of $Fe(OH)_2$, and before pptg. Group III. the iron is always oxidised to the ferric state.

2. **KOH** ppts. $Fe(OH)_2$ is in 1. Excess of alkali does not dissolve it.

3. **Alkali carbonates** ppt. white $FeCO_3$, which is, however, readily hydrolysed and oxidised.

4. **$K_4Fe(CN)_6$** with absolutely ferrous salts ppts. white ferrous ferrocyanide, $Fe_2[Fe(CN)_6]$. It immediately absorbs oxygen, turning blue. Hence the usual result is a more or less pale blue ppt.

5. **$K_3Fe(CN)_6$** ppts. dark blue ferrous ferricyanide.

$$Fe_3[Fe(CN)_6]_2 \text{ or Turnbull's blue.}$$

There is some doubt about the exact composition of Prussian and Turnbull's blue. It is probable that both are the same substance, *viz.* ferric ferrocyanide. If, however, the ferro or ferricyanide is in excess the product is $KFeFe(CN)_6$ "soluble" Prussian or Turnbull's blue.

6. **KCNS** has no visible reaction.

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7. **Alkali sulphides** ppt. black FeS soluble in dilute acids. *Hydrogen sulphide* in neutral solution may ppt. a little black FeS, which is, however, soluble in the acid produced by the reaction.

8. **KCN** ppts. ferrous cyanide (?) soluble in excess to form $K_4Fe(CN)_6$. A blue ppt. is generally obtained on adding KCN to a ferrous salt, the reason being obvious. (See 4 above.)

II. Ferric Salts.

Ferrous salts are oxidised to ferric salts in acid solution by most oxidising agents, including dissolved oxygen. Strong nitric acid is the most convenient. In absence of excess of acid, an insoluble basic ferric salt is produced.

$$2FeSO_4 + H_2SO_4 + O(\text{from oxidiser}) = Fe_2(SO_4)_3 + H_2O.$$
$$2FeSO_4 + H_2O + O = 2Fe(OH)SO_4.$$

Most ferric salts are yellow in solution.

1. **NH_4OH** ppts. red-brown $Fe(OH)_3$, insoluble in ammonium salts.
2. **KOH** ppts. $Fe(OH)_3$, insoluble in excess of the reagent.
3. **Alkali sulphides** ppt. ferrous sulphide and sulphur.

$$2FeCl_3 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$

Hydrogen sulphide in neutral or acid solution is oxidised to sulphur, the ferric salt being reduced to ferrous. $2FeCl_3 + H_2S = 2HCl + 2FeCl_2 + S$.

Many other reducing agents also reduce ferric salts to ferrous, *e.g.* HI, $SnCl_2$, SO_2, nascent hydrogen.

4. **Alkali carbonates, $BaCO_3$, etc., and basic oxides and hydroxides of the divalent metals** ppt. $Fe(OH)_3$, the action being hydrolytic. All ferric salts are slightly hydrolysed in aqueous solution.

$$FeCl_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3HCl.$$

The HCl is removed by the carbonate or base, and the Mass Law does the rest.

5. **$K_4Fe(CN)_6$** ppts. dark blue ferric ferrocyanide, or Prussian blue. $Fe_4''' [Fe'' (CN)_6]_3$ is the ideal compound, but it usually still contains more or less potassium, $KFe''' [Fe'' (CN)_6]$.

6. **$K_3Fe(CN)_6$** (which should be freshly made) gives a brown colour with ferric salts.

N.B.—Since ferrocyanides and ferricyanides do not give any of the wet reactions for iron, they must be transformed for analysis either by heat alone or better by heating with fusion mixture,

e.g. $$2K_3[Fe(CN)_6] = 6KCN + FeC_2 + N_2 + C_2N_2$$
or $$K_4[Fe(CN)]_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe.$$

In either case extract the melt with water and dissolve the residue in dilute hydrochloric acid.

7. **KCNS** gives a blood-red colour of $Fe(CNS)_3$, except in the presence of mercuric chloride, which reacts with it and forms a complex mercuric compound $6HgCl_2 + 2Fe(CNS)_3 = 2FeCl_3 + 3[Hg(CNS)_2, HgCl_2]$.

8. **Alkali acetates** give a reddish-brown colour of ferric acetate. On

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boiling, hydrolysis takes place, and if the solution is sufficiently dilute, all the iron is pptd. as a basic acetate. (Separation from manganese.) *Cf.* chromium and aluminium

$$Fe(C_2H_3O_2)_3 + 2H_2O = 2H(C_2H_3O_2)_2 + Fe(OH)_2(C_2H_3O_2).$$

9. **Na_2HPO_4** ppts. pale yellow ferric phosphate, $FePO_4$, insoluble in acetic acid.

MANGANESE, Mn = 55.

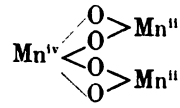
Oxides.—MnO basic, unstable, readily oxidised. Mn_2O_3 has slight basic properties. The action of nitric acid is to form manganous nitrate and leave manganese dioxide, thus showing it to be meta-manganous manganite; $Mn^{iv}O(OMn^{ii})$.

$$Mn_2O_3 + 2HNO_3 = Mn(NO_3)_2 + MnO(OH)_2.$$

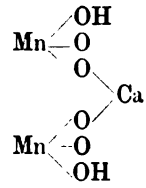
Mn_3O_4 reacts similarly with nitric acid, giving up two thirds of its manganese.

$$Mn_3O_4 + 4HNO_3 = H_2O + 2Mn(NO_3)_2 + MnO(OH)_2.$$

It is thus to be regarded as orthomanganous manganite.



MnO_2 is a peroxide, also an acid anhydride; the above two oxides are two of its salts; Weldon mud is to be regarded as calcium bimanganite.



MnO_3 is very unstable, but salts corresponding to it are well defined, *e.g.* potassium manganate, K_2MnO_4.

Mn_2O_7 permanganic anhydride. All the oxides by ignition in air form Mn_3O_4.

The manganese salts fall into two classes, manganous salts and the salts of manganic and permanganic acid. The manganic salts are rare and unstable, and probably manganic rubidium alum is the only one known with certainty, other manganese alums being at the best very unstable and easily hydrolysed.

Dry Tests.

Heated on charcoal before the blowpipe a brown residue of Mn_2O_3 is obtained. Permanganates are reduced with deflagration.

Fused with alkali on platinum foil, all manganese compounds are oxidised (by air or better by a crystal of potassium nitrate or chlorate) to manganates,

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a green melt being obtained, giving a fine green solution in water which rapidly turns to permanganate (purple).

$$MnO + Na_2CO_3 + O_2 = CO_2 + Na_2MnO_4$$
$$MnO_2 + Na_2CO_3 + O = CO_2 + Na_2MnO_4$$

etc. This reaction is very delicate.

The borax bead is coloured amethyst in the oxidising flame, colourless in the reducing flame, by all manganese compounds. It is somewhat difficult to obtain a colourless bead if the compound used is in a higher state of oxidation than mangan*ous*.

Wet Tests.

I. Manganous Compounds.

All soluble hydrated salts are pink, anhydrous and insoluble ones white, except the sulphide.

1. **NH_4OH** ppts. white $Mn(OH)_2$, soluble in ammonium chloride. Unless this salt is first added, only half of the $Mn(OH)_2$ dissolves.

$$2MnCl_2 + 4NH_4OH = 2Mn(OH)_2 + 4NH_4Cl.$$
$$4NH_4Cl + Mn(OH)_2 = (NH_4)_2MnCl_4 + 2NH_4OH.$$

The $Mn(OH)_2$ is very readily oxidised to $MnO(OH)_2$ by atmospheric oxygen or by the usual oxidising agents (H_2O_2, Cl_2, Br_2, hypochlorites, etc.). Even as the "double" salt $(NH_4)_2MnCl_4$ it is readily oxidised, so that on filtering off the ppt. (by NH_4OH) the solution rapidly ppts. $MnO(OH)_2$.

$$(NH_4)_2MnCl_4 + 2NH_4OH + O = 4NH_4Cl + MnO(OH)_2$$

(See also formation of *Weldon mud.*)

2. **KOH** ppts. $Mn(OH)_2$, insoluble in the reagent, readily oxidised as in 1.

3. **Alkali sulphides** ppt. flesh-coloured $MnS + aq$. If this is boiled with much ammonium sulphide a less hydrated green sulphide is obtained. MnS is soluble in dilute acids.

4. **Alkali carbonates** ppt. white $MnCO_3$.

5. **Volhard's Reaction.**—If a manganous salt (other than halides) is boiled with much dilute nitric acid and a pinch of red lead or lead dioxide added and allowed to settle, the liquid is coloured purple, due to the formation of permanganic acid

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2H_2O + 2PbSO_4 + 3Pb(NO_3)_2.$$

Oxidation of manganous compounds.

In the presence of alkali, manganous hydroxide is rapidly oxidised by atmospheric oxygen and by the halogens, hypochlorites, etc., to manganese dioxide (hydrated), or in the presence of salts of the divalent metals, Ba, Sr, Ca, Zn, etc., to manganites or bimanganites. A well-known example of this is the Weldon process for the recovery of manganese dioxide for the manufacture of chlorine.

The residues are treated with excess of milk of lime.

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2.$$

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Steam and air are blown in

$$2Mn(OH)_2 + Ca(OH)_2 + O_2 = \begin{array}{l} Mn\begin{cases} OH \\ -O \\ O \end{cases} \\ \qquad\qquad\qquad Ca + 2H_2O. \\ Mn\begin{cases} O \\ =O \\ OH \end{cases} \end{array}$$

i.e. the acid calcium salt of $MnO(OH)_2$. The *oxidation* may be simply schemed as

$$Mn(OH)_2 + O = \underset{\text{black}}{MnO(OH)_2}.$$

If air is the oxidising agent, it is probable that the manganous hydroxide goes through various intermediate stages of oxidation corresponding to Mn_3O_4, Mn_2O_3 and finally MnO_2.

Recognition of MnO_2.

1. **Heat** causes evolution of oxygen at a high temperature.

$$3MnO_2 = Mn_3O_4 + O_2.$$

2. **Strong H_2SO_4** causes evolution of oxygen on being heated.

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

3. **Strong HCl** forms a green solution (probably $MnCl_4$) which when heated gives chlorine.

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O$$
$$MnCl_4 = MnCl_2 + Cl_2.$$

4. **Oxalic acid** is oxidised in acid solution to CO_2.

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = 2H_2O + 2CO_2 + MnSO_4.$$

Ferrous salts are similarly oxidised to ferric salts, HBr and HI to bromine and iodine, etc.

II. Manganates and Permanganates.

Manganates are formed when MnO_2 is fused with alkali and an oxidising agent (KNO_3, $KClO_3$, or the air).

$$MnO_2 + 2KOH + O = K_2MnO_4 + H_2O.$$

They are stable only in alkaline solution. The free acid at once oxidises part of itself to permanganic acid the rest of it being thereby reduced to manganese dioxide (hydrate).

$$3H_2MnO_4 = 2HMnO_4 + MnO(OH)_2 + H_2O.$$

Hence permanganates are made by acidifying the manganate solution made as above. The acid used on the small scale is CO_2. On the large scale, to prevent loss of manganese as MnO_2, the transformation is effected by ozone, which oxidises the manganate to permanganate. (See p. 61).

Permanganic acid is only known in aqueous solution, but the anhydride Mn_2O_7 is formed as brown oil when cooled strong sulphuric acid is carefully

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added to permanganate crystals. It is explosive when warmed gently (care !). $Mn_2O_7 + 2H_2SO_4 = 2H_2O + 2MnSO_4 + 5O$.

Permanganates and permanganic acid are recognised by the characteristic colour of their solutions and by the oxidising and reducing actions when treated with various reagents, as indicated below.

Permanganates give off oxygen when the dry powder is heated.

$$2KMnO_4 = K_2O + 2MnO_2 + 3O.$$

The halogen acids are readily oxidised in the cold, and this forms a very convenient preparation of chlorine when only a small quantity is required.

The oxidising actions of permanganates fall under three heads, according to the stage to which they are reduced.

The oxidation in *acid* solution is represented by the scheme :

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + MnSO_4 + 5O.$$

In *alkaline* solution they are reduced either to manganates or to manganese dioxide, according to the vigour of the reducing agent. Schemes :

(i) $2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O.$

(ii) $2KMnO_4 + 2H_2O = 2KOH + O_2 + 2MnO(OH)_2.$

The following substances are oxidised in acid solution by $KMnO_4$; the equations are left to the student.

Oxalic acid (CO_2 and water).

Hydrogen peroxide ($H_2O + O$; the O unites with O from the permanganate to form a molecule of oxygen).

Ferrous salts (ferric salts).

Hydriodic acid (iodine and water).

Hydrogen sulphide ($H_2O + S$).

Hydrogen chloride and bromide ; the strong acids in the cold, the dilute ones on warming. Many organic substances reduce permanganate both in acid and alkaline solution. (See under tartaric and citric acids.)

ZINC, Zn = 65·3.

Oxide. ZnO, basic ; (acidic to caustic potash and soda).

Dry Tests.

Compounds of zinc which are changed to oxide on ignition give an incrustation on charcoal which is yellow when hot, white when cold (very characteristic of ZnO). This, when moistened with cobalt nitrate and strongly heated yields a green mass (Rinmann's green). It is impossible to obtain metallic zinc on charcoal, as the metal is readily volatile.

Wet Tests.

Use a solution of zinc sulphate.

1. **NH_4OH** ppts. white $Zn(OH)_2$, readily soluble in both ammonium salts and ammonia itself. In the former it dissolves as do the hydroxides of

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nickel, manganese, magnesium, etc., *q.v.* In the latter it behaves as copper hydroxide does.

$$Zn(OH)_2 + 4NH_4Cl = (NH_4)_2ZnCl_4 + 2NH_4OH$$

or

$$Zn(OH)_2 + 6NH_3 = [Zn(NH_3)_6](OH)_2.$$

2. **KOH** ppts. $Zn(OH)_2$ easily soluble in excess, forming a zincate.

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O.$$

It is not hydrolysed by boiling if sufficient alkali be present, nor is it decomposed by boiling with ammonium chloride (*cf.* aluminium).

3. **Alkali sulphides** ppt. white ZnS, which is very ready to assume a colloidal state. It must be pptd. from a hot solution in presence of ammonium salts to prevent this. ZnS is insoluble in acetic, soluble in mineral acids.

4. **Na_2HPO_4** ppts. white $Zn_3(PO_4)_2$ soluble in ammonia and in ammonium chloride.

5. **Na_2CO_3** ppts. a white basic carbonate. (The normal carbonate is pptd. by $NaHCO_3$). Ammonium carbonate does the same, but the ppt. is soluble in excess of the reagent and in ammonium salts.

NICKEL, Ni = 58·7.

Oxides.—NiO basic.

Ni_2O_3 (?) peroxide. (See *Text-book of Inorganic Chemistry*, Friend (Griffin), Vol. IX. Pt. I. p. 117).

Both oxides give rise, therefore, to nickel*ous* salts when dissolved in acids, *e.g.* $Ni_2O_3 + 6HCl = 2NiCl_2 + 3H_2O + Cl_2$.

Soluble nickel salts are green in the crystalline state, yellow when anhydrous. Most of the insoluble compounds (as carbonate, etc.) are green.

Nickel is not easily soluble in hydrochloric or sulphuric acids, but readily in nitric.

Dry Tests.

Heated on charcoal by the blowpipe, with or without fusion mixture, black magnetic scales of metallic nickel are obtained. The charcoal stick gives a similar reaction. The borax bead is coloured yellow-brown in the oxidising flame, grey and opaque in the reducing flame, due to separation of fine particles of metallic nickel.

Wet Tests.

Use a solution of nickel sulphate or nitrate.

1. **NH_4OH** ppts. a green basic salt, soluble in excess to a blue solution (*cf.* copper).

$$2NiSO_4 + 2NH_4OH = (NH_4)_2SO_4 + Ni_2(OH)_2SO_4,$$

and then

$$Ni_2SO_4(OH)_2 + (NH_4)_2SO_4 + 10NH_3 = 2[Ni(NH_3)_6]SO_4 + 2H_2O.$$

If ammonium salts are present, no ppt. is formed, for

$$NiCl_2 + 2NH_4Cl = (NH_4)_2[NiCl_4],$$

which readily adds on ammonia to form nickel ammonia compounds, *e.g.* $[Ni(NH_3)_6]Cl_2$ (see p. 31).

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2. **KOH** ppts. apple-green $Ni(OH)_2$. This is readily oxidised by chlorine, bromine, hydrogen peroxide, hypochlorites, etc., to black $Ni(OH)_3$.*

$$2Ni(OH)_2 + 2NaOH + Cl_2 = 2NaCl + 2Ni(OH)_3.*$$

3. **$(NH_4)_2S$** ppts. black NiS, forming a black colloidal solution with excess of yellow ammonium sulphide. To prevent this, it is necessary to ppt. NiS by passing hydrogen sulphide into an ammoniacal solution. Though the presence of free mineral acid will entirely prevent the pptn. of NiS, yet pptd. NiS is very difficult to dissolve in dilute mineral acid. The solvent for it is aqua regia.

4. **Alkali carbonates** ppt. green $NiCO_3$. Ammonium carbonate in excess redissolves this ppt.

5. **KCN** ppts. pale green nickelous cyanide, $Ni(CN)_2$ readily soluble in excess of the reagent, forming potassium nickelocyanide.

$$Ni(CN)_2 + 2KCN = K_2[Ni(CN)_4]$$

(difference from cobalt).

This is decomposed by dilute acids, repptg. $Ni(CN)_2$, which is not readily soluble in cold dilute acid.

$K_2[Ni(CN)_4]$ is not acted on by ammonium sulphide (difference from Mn and Zn) but is readily decomposed by treating with Cl_2, Br_2, hypochlorites, etc., in alkaline solution. Large excess of potassium cyanide hinders the reaction, as it prevents the decomposition of the nickelo-cyanide (mass action, see p. 30).

$$K_2[Ni(CN)_4] + 4Cl_2 = 2KCl + NiCl_2 + \underset{\text{cyanogen chloride.}}{4CNCl}.$$

$$NiCl_2 + 2NaOH = Ni(OH)_2 + 2NaCl.$$

$$2Ni(OH)_2 + H_2O + NaOCl = 2Ni(OH)_3* + NaCl.$$

Bromine acts similarly, but not so readily. Hence we may detect traces of nickel in cobalt salts, provided that undue excess of KCN be avoided.

6. **Na_2HPO_4** ppts. $Ni_3(PO_4)_2$ soluble in acetic acids.

7. **KNO_2** produces no ppt. in dilute solutions (*cf.* cobalt).

8. **α-Dimethyl glyoxime** (alcohol solution) ppts. bulky scarlet $C_8H_{14}N_4O_4Ni$. **α-Diphenyl glyoxime** is more sensitive, giving a bulky red ppt. of $C_{28}H_{22}N_4O_4Ni$.

COBALT, Co = 59·0.

Oxides.—CoO basic. Gives rise to cobaltous salts.

Co_3O_4 compound of the other two oxides. Gives rise to cobaltous and cobaltic salts with dilute acids.

Co_2O_3 basic to cold acids, peroxide to hot acids. Gives rise to cobaltic salts with cold acids, cobaltous with hot acids.

$$CoO + 2HCl = CoCl_2 + H_2O.$$

$$Co_2O_3 + 6HCl = 2CoCl_3 + 3H_2O \text{ (cold).}$$

$$Co_2O_3 + 6HCl = 2CoCl_2 + 3H_2O + Cl_2 \text{ (hot).}$$

$$Co_3O_4 + 8HCl = CoCl_2 + 2CoCl_3 + 4H_2O \text{ (cold).}$$

etc.

The solvent for metallic cobalt is nitric acid.

* There is some doubt as to the composition of this ppt.

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Dry Tests.

The reaction on charcoal or the charcoal stick is indistinguishable from that of nickel. Cobalt also is magnetic.

The borax bead is coloured blue both in the oxidising and reducing flames.

Soluble cobalt salts are deep pink when hydrated, blue when anhydrous, or in presence of much HCl. Most insoluble compounds are blue.

Wet Tests.

Use a solution of cobalt nitrate.

1. **NH_4OH** ppts. first a blue basic salt

$$NH_4OH + Co(NO_3)_2 = Co(OH)NO_3^* + NH_4NO_3,$$

which is soluble in excess of ammonium chloride (*cf.* nickel). The cobalt is, however, slowly oxidised by atmospheric oxygen to the cobaltic state, and the yellow solution turns reddish.

2. **KOH** ppts. first a blue basic salt as above.* This is decomposed by more hot KOH, and pink $Co(OH)_2$ is formed. This, however, gradually absorbs oxygen from the air, turning brown and finally black.

$$2Co(OH)_2 + O + H_2O = 2Co(OH)_3$$

(*cf.* iron, manganese and nickel).

Cobaltous hydroxide is very readily oxidised in presence of alkalis by the halogens, hypochlorite, etc.

3. **$(NH_4)_2S$** ppts. black CoS, insoluble in ammonium sulphide and dilute mineral acids, soluble in aqua regia. Though the presence of dilute mineral acids prevents the pptn. of cobalt sulphide, yet when pptd. it is practically insoluble therein (*cf.* nickel). The reason for this is probably that polymerisation occurs and a large molecule $(CoS)_n$ is formed.

4. **$BaCO_3$** in the cold and absence of air ppts. no cobalt. If, however, an oxidising agent (Br_2aq, H_2O_2, etc.) be added, the cobalt is oxidised and pptd. as $Co(OH)_3$ (*cf.* nickel and ferric iron).

5. **Alkali carbonates** ppt. a basic carbonate of varying composition (soluble in *ammonium* carbonate).

6. **KCN** ppts. brownish $Co(CN)_2$, soluble in excess, forming a brown solution of potassium cobalto-cyanide.

$$CoCl_2 + 2KCN = Co(CN)_2$$
$$Co(CN)_2 + 4KCN = K_4[Co(CN)_6] \text{ (cf. Ni).}$$

When this solution is warmed in the air it absorbs oxygen and turns yellow :

$$2K_4Co(CN)_6 + O + H_2O = 2KOH + \underset{\text{cobalticyanide.}}{2K_3[Co(CN)_6]}.$$

Note that cobalt here reacts much more like iron than does nickel. No analogous compounds of nickel exist.

The above oxidation is rapidly completed by addition of the usual oxidising agents, and an excess of chlorine, etc., does not decompose the cobalticyanide,

* There is some doubt as to the composition of this ppt.

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neither do dilute mineral acids. The cobaltocyanide, however, is decomposed by dilute acids.

$$K_4Co(CN)_6 + 4HCl = 4KCl + 4HCN + Co(CN)_2.$$

Potassium cobalticyanide is analogous in its reactions to potassium ferricyanide. Note especially its reactions with nickelous and cobaltous salts, with which it forms green nickelous and pink cobaltous cobalticyanides.

Hence nickel may be detected in presence of cobalt by adding KCN till ppts. just dissolve, boiling to oxidise to cobalticyanide, and then adding hydrochloric acid, when green nickel cobalticyanide is pptd.

7. **KNO_2** followed by acetic acid ppt. yellow potassium cobaltinitrite. (In dilute solution after standing.)

Reactions:

1. $CoCl_2 + 2KNO_2 = Co(NO_2)_2 + 2KCl.$
2. $2KNO_2 + 2H(C_2H_3O_2) = 2KC_2H_3O_2 + 2HNO_2.$

Oxidation.
3. $Co(NO_2)_2 + 2HNO_2 = Co(NO_2)_3 + NO + H_2O.$
4. $Co(NO_2)_3 + 3KNO_2 = K_3[Co(NO_2)_6].$

8. **$(NH_4)CNS$** (Vogel's reaction) gives, with strong solutions, a fine blue colour of $(NH_4)_2[Co(CNS)_4]$, which disappears on dilution (double salt separated into its constituent salts).

On the addition of a mixture of amyl alcohol and ether and shaking well, the blue compound dissolves in the upper alcoholic layer, which is coloured blue. This reaction is exceedingly sensitive, and serves for the detection of traces of cobalt in nickel salts, provided that iron is absent; the red $Fe(CNS)_3$ interfering. Iron may, however, be pptd. *after* the addition of the alcohol-ether layer, by adding sodium carbonate solution.

The blue sulphocyanate solution in amyl alcohol-ether has a very characteristic absorption spectrum. Observe it. Also note the flames of sodium potassium, barium, strontium, and calcium through the solution, and explain what you see. Cobalt glass has a somewhat similar absorption spectrum and is similarly used.

9. **α-Nitroso β-naphthol** ppts. red cobaltinitroso β-naphthol from solutions of cobalt salts acidified with acetic acid. (Complete separation from nickel.)

GROUP IV.

Group reagent, $(NH_4)_2CO_3$ in presence of NH_4Cl.

BARIUM, STRONTIUM, CALCIUM.

These three metals are chemically very much alike, and the separation depends merely on differences in solubility between various very similar salts.

BARIUM, Ba = 137·4.

Oxides: BaO basic; BaO_2 peroxide.

BaO, when heated to a dull red heat, takes in oxygen and forms BaO_2,

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which on being strongly heated gives up its oxygen again. (Brin's oxygen process.)

$$2BaO + O_2 \underset{\text{bright red.}}{\overset{\text{dull red.}}{\rightleftharpoons}} 2BaO_2.$$

BaO_2 treated with dilute acid gives H_2O_2.

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2.$$

Treated with strong HCl it gives oxygen (and some chlorine) and with strong sulphuric acid oxygen and some ozone.

Dry Tests.

On charcoal before the blowpipe, all barium salts which are converted to oxide give a white infusible residue, not very luminous when hot (*cf.* Sr and Ca). No colour test is given with cobalt nitrate.

Moistened with dilute hydrochloric acid, barium salts impart a pale apple-green colour to the flame. The spectrum of barium has broad bright lines in the orange, yellow and green.

Wet Tests.

1. **$(NH_4)_2CO_3$** ppts. white $BaCO_3$, which settles and filters much better after boiling the liquid. It is insoluble in NH_4Cl. $BaCO_3$ is very difficult to decompose by heat alone.

2. **KOH** ppts. white $Ba(OH)_2$, insoluble in excess, from moderately strong solutions (solubility of $Ba(OH)_2 = 3{\cdot}7$ at 18°C).

3. **Sulphuric acids** and soluble sulphates ppt. white $BaSO_4$, insoluble in acids except hot strong H_2SO_4, which produces a bisulphate $Ba(HSO_4)_2$.

4. **$CaSO_4$** *immediately* ppts. $BaSO_4$.

5. **K_2CrO_4** ppts. lemon-yellow $BaCrO_4$, insoluble in acetic, soluble in mineral acids. $K_2Cr_2O_7$ also ppts. the chromate, though incompletely (for obvious reasons) except in presence of sodium acetate.

6. **$(NH_4)_2C_2O_4$** ppts. white BaC_2O_4 even in presence of acetic acid, unless the solution is dilute.

STRONTIUM, Sr = 87·6.

Oxide, SrO. Basic.

Dry Tests.

On charcoal, before the blowpipe, a white infusible residue is obtained, more highly luminous when hot than that from barium (more readily reduced to oxide).

Moistened with dilute hydrochloric acid, strontium salts colour the flame crimson. Viewed through cobalt glass the flame appears purple (difference from Ca). The spectrum shows red lines and one in the blue.

Wet Tests.

1. **$(NH_4)_2CO_3$** as with barium.

2. **KOH** ppts. white $Sr(OH)_2$ if the solution is strong enough.

3. **Sulphuric acid and soluble sulphates** ppt. white $SrSO_4$, insoluble in acids, as is $BaSO_4$. The solubility of $SrSO_4$ is, however, much greater than that of

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$BaSO_4$. Consequently, in dilute solutions the ppt. is often delayed for some time, *especially by HCl.*

4. **$CaSO_4$** ppts. $SrSO_4$ after standing for some time, but *not* if much HCl is present.

5. **K_2CrO_4** ppts. yellow $SrCrO_4$ from *strong neutral* solutions only.

6. **$(NH_4)_2C_2O_4$** ppts. white SrC_2O_4, even in presence of acetic acid, unless the solution is dilute.

CALCIUM, Ca = 40·1

Oxide, CaO. Basic. Readily takes up moisture, forming $Ca(OH)_2$.

Dry Tests.

On charcoal before the blowpipe most Ca salts leave a residue of CaO, highly luminous when hot. If mixed with fusion mixture, *all* calcium salts do this.

Moistened with dilute hydrochloric acid, calcium salts colour the flame brick-red. It is easy, especially for beginners, to mistake the calcium for the strontium flame, *unless the two are seen together.* An easy differentiation, however, is made by looking at the flame through cobalt glass (potassioscope), when it appears *green* (*cf.* strontium).

The calcium spectrum contains lines in the orange and yellow and one in the green.

Wet Tests.

1. **$(NH_4)_2CO_3$** ppts. white $CaCO_3$, which settles better on boiling the liquid.

2. **KOH** ppts. white $Ca(OH)_2$ except from dilute solutions.

3. **H_2SO_4** ppts. white $CaSO_4$ from fairly strong solutions not containing hydrochloric acid. *$CaSO_4$ is readily soluble in HCl.* If the solution is very dilute, alcohol as well as H_2SO_4 should be added.

4. **K_2CrO_4** gives no reaction.

5. **$(NH_4)_2C_2O_4$** ppts. white CaC_2O_4 quantitatively from neutral or alkaline solutions, or from *acetic* acid solutions. In the cold the ppt. is very fine and difficult to filter. If pptd. at the boiling point it is much denser and larger in grain. This is generally true of all insoluble salts of the alkaline earths.

GROUP V.

No group reagent.

Magnesium, Potassium, Sodium, Ammonium (Lithium Rubidium, Caesium).

MAGNESIUM, Mg = 24·2.

Oxide. MgO. Basic.

Solvent for metal, dilute hydrochloric acid.

Dry Tests.

On charcoal with the blowpipe, a white infusible residue of MgO, luminous when hot, is left by many magnesium compounds, by all if fusion mixture

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is employed. This, moistened with cobalt nitrate and heated strongly, forms a pink mass.

Magnesium compounds give no flame-spectrum, but a characteristic spark spectrum.

N.B.—Magnesium carbonate (native) does not evolve carbon dioxide with cold dilute acids. In this respect it is practically unique. It reacts in the usual way, however, when heated. The dry solid gives up its carbon dioxide far more readily than any other of the alkali-earth carbonates when heated.

Wet Tests.

Use a solution of magnesium sulphate, $MgSO_4$, $7H_2O$.

1. **NH_4OH** ppts. white $Mg(OH)_2$, soluble in ammonium salts to form a complex salt.

$$Mg(OH)_2 + 4NH_4Cl = (NH_4)_2MgCl_4 + 2NH_4OH.$$

Thus *half* the $Mg(OH)_2$ pptd. by ammonia will be dissolved by the ammonium chloride, etc., formed at the same time.

$$MgCl_2 + 2NH_4OH = Mg(OH)_2 + 2NH_4Cl.$$

2. **KOH** ppts. white $Mg(OH)_2$ insoluble in excess.

3. **Alkali carbonates** ppt. white voluminous $MgCO_3$. If ammonium carbonate be used, half the carbonate will be dissolved in the ammonium salt formed. Hence magnesium does not come in Group IV. being dissolved by the ammonium chloride present.

4. **Na_2HPO_4**, in the presence of ammonium chloride and ammonia, ppts. white crystalline $MgNH_4PO_4$, $6H_2O$. From dilute solutions pptn. may take some time, and is hastened by gently rubbing the sides of the test-tube with a glass rod. It may also be mentioned that microcosmic salt is a more sensitive reagent for this test than Na_2HPO_4.

Magnesium ammonium phosphate is a very characteristic ppt., and a little of it, suspended in a drop of the liquid, should be examined with a microscope ($\frac{1}{6}''$ objective).

Note also the corresponding arsenate.

POTASSIUM, K = 39·15.

Oxides. K_2O ? basic. K_2O_4 peroxide.

Dry Tests.

Heated on charcoal, potassium salts fuse and sink into the charcoal, except the phosphate and borate, which remain as a fused bead.

Potassium compounds, especially if moistened with dilute hydrochloric acid, colour the flame lilac. The spectrum consists of a red and a violet line. The flame of potassium viewed through cobalt glass, appears much the same colour as when viewed directly.

Wet Tests.

Use a fairly strong solution of potassium chloride.

No potassium salt is insoluble in water: the solubility of some, however, is sufficiently limited to give a pptn. test in moderately strong solution.

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1. **Perchloric acid, $HClO_4$** ppts. white crystalline $KClO_4$ (solubility at 0° C. = ·07).

2. **Sodium bitartrate or tartaric acid** ppt. white crystalline $KHC_4H_4O_6$, especially on rubbing the sides of the test-tube with a glass rod. The ppt. first appears along the scratches.

$$KCl + H_2(C_4H_4O_6) = \underset{\text{(cream of tartar)}}{KH(C_4H_4O_6)} + HCl.$$

As cream of tartar is very readily soluble in mineral acids, it is necessary to add some sodium acetate if tartaric acid is used, to replace the hydrochloric formed by acetic.

3. **H_2PtCl_6** ppts. yellow crystalline H_2PtCl_6 from fairly strong solutions, especially on rubbing the tube as before. It is practically insoluble in alcohol.

K_2PtCl_6 on ignition decomposes thus:

$$K_2PtCl_6 = 2KCl + Pt + 2Cl_2.$$

N.B.—With potassium iodide the reaction is uncertain, owing to the reduction of the chlorplatinic acid to chlorplatinous.

$$H_2PtCl_6 + 2KI = H_2PtCl_4 + 2KCl + I_2.$$

Hence to test an iodide for potassium, first convert to chloride by evaporation with hydrochloric acid.

4. **Sodium picrate** *in presence of sodium carbonate* ppts. yellow crystalline potassium picrate. This is one of the best tests for potassium. The picrate solution should be saturated and should contain sodium carbonate, and the potassium solution must be *free from ammonium salts* (*q.v.*)

5. **Carnot's reaction**—To a few drops of a solution of $Bi(NO_3)_3$ add a few drops of sodium thiosulphate and several c.cs. of alcohol. A double salt, $Na_3[Bi(S_2O_3)_3]$, is formed, which with solutions of potassium salts forms the corresponding potassium salt as a canary-yellow ppt.

Ammonium salts must be absent.

6. **De Koningh's reagent, $Na_3[Co(NO_2)_6]$**, ppts. yellow $K_3[Co(NO_2)_6]$. (See under cobalt.)

7. **H_2SiF_6** in excess ppts. gelatinous K_2SiF_6, except with KOH and K_2CO_3, when a ppt. of silicic acid is formed.

8. Potassium peroxide gives a rapid evolution of oxygen when treated with water.

SODIUM, Na = 23·05.

Oxides. Na_2O (?) *basic.* Na_2O_2 *peroxide.*

Dry Tests.

Heated on charcoal, sodium salts melt and run into the charcoal, except the phosphates and borates, which give a fused bead.

The flame is coloured intense yellow by all sodium compounds, especially when moistened with dilute hydrochloric acid. Viewed through cobalt glass

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the sodium flame is invisible, as this particular yellow is absorbed by cobalt blue. Hence the potassium flame can be seen in the presence of the sodium flame by using the glass. It is an exceedingly delicate test for potassium, however, and must therefore be used with caution by the student. With cobalt glass it is possible to detect potassium in *puriss.* anhydrous sodium carbonate. A pptn. test for potassium should therefore always be obtained as well as the flame test.

Wet Test.

1. **$K_2H_2Sb_2O_7$** (pyroantimoniate) produces in neutral solutions a heavy white crystalline ppt. of the sodium salt (Rub). The solution tested must not be acid, or pyroantimonic acid is pptd., and no other metal than the alkalis must be present. The reagent solution should be freshly prepared.

SODIUM PEROXIDE.

Na_2O_2 is much used as an oxidising agent. Treated with water, it reacts thus:

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2,$$

and the heat of the reaction decomposes most of the H_2O_2, causing a violent evolution of oxygen, unless the heating up of the solution is avoided.

The reactions of hydrogen peroxide are given here.

H_2O_2.

I. *In acid solution.*

1. **Chromic acid** gives a blue colour, soluble in ether. (See under Chromic acid.)

2. **Titanium sulphate** gives a yellow colour.

(Make the titanium sulphate by fusing commercial TiO_2 with considerable excess of $KHSO_4$, and dissolving the melt in cold dilute sulphuric acid.

3. **$HMnO_4$** is decolorised with evolution of oxygen.

$$2KMnO_4 + 3H_2SO_4 + 4H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Many oxides are also reduced by H_2O_2, *e.g.*, Ag_2O, PbO_2, etc.

4. **MnO_2** decomposes H_2O_2 catalytically.

II. *In alkaline solution.*

1. **Many metallic hydroxides**, especially $Mn(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$ and $Fe(OH)_2$ are oxidised by H_2O_2 as we have seen under each metal.

2. **$AuCl_3$** is *reduced* to Au, with evolution of oxygen. The gold appears as a brown or greenish colloidal solution.

$$3H_2O_2 + 2AuCl_3 + 6NaOH = 6NaCl + 6H_2O + 3O_2 + 2Au.$$

AMMONIUM, NH_4.

Ammonium salts show a great resemblance to potassium salts in all their wet tests.

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Dry Tests.

On charcoal all ammonium salts are completely volatile, with or without decomposition, except those of non-volatile acids, in which case the acid or acid anhydride will be left.

Such are the phosphate, borate, chromate, molybdate, vanadate and tungstate. Ammonium salts of oxyacids often suffer complete decomposition when heated in a dry tube. Thus the nitrate gives off N_2O and water, the dichromate gives nitrogen, water and a residue of chromic oxide, Cr_2O_3, and the sulphate gives nitrogen, ammonia, water and sulphur dioxide.

$$NH_4NO_3 = 2H_2O + N_2O.$$
$$NH_4NO_2 = 2H_2O + N_2.$$
$$3(NH_4)_2SO_4 = N_2 + 4NH_3 + 6H_2O + 3SO_2.$$
$$(NH_4)_2Cr_2O_7 = 4H_2O + N_2 + Cr_2O_3.$$

All ammonium salts ground in a mortar with lime give off ammonia (difference from amides).

Wet Tests.

1. **NaOH or KOH** solution, boiled with ammonium salts, give off ammonia. (Amides also give off ammonia when thus treated.)

2. **H_2PtCl_6** ppts. yellow $(NH_4)_2PtCl_6$ very similar to the potassium salt. On ignition, however, platinum only is left.

$$(NH_4)_2PtCl_6 = 2NH_3 + 2HCl + 2Cl_2 + Pt.$$

3. **Tartaric acid or $NaH(C_4H_4O_6)$** as with potassium.

4. **Sodium picrate** ($+ Na_2CO_3$) also gives a ppt. resembling the corresponding potassium salt.

5. **Nessler's reagent** (a solution of mercuric potassium iodide in excess of potash) gives a brown ppt. If ammonia is present in small quantity only, a yellow coloration is obtained.

This is one of the most delicate reactions in inorganic chemistry. By means of this reagent ammonia is readily distinguished in ordinary distilled water, and the reagent is employed in *estimating* ammonia rather than in detecting it.

LITHIUM, Li = 7·03.

Lithium is the commonest of the rare alkali metals. It occurs in petalite and lepidolite and many other silicates, whence it gets into many mineral-spring waters. It can sometimes be detected in tobacco-ash.

Dry Tests.

On charcoal, as with other alkali metals. The flame test gives a magnificent crimson flame; in presence of sodium it is observed through cobalt glass. The spectrum consists of a brilliant red line and a faint orange one.

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Wet Tests.

Use a solution of lithium chloride.

1 and 2. Neither **H_2PtCl_6** nor **tartaric acid** give ppts.

3. **Na_2HPO_4** ppts. white Li_3PO_4 from fairly strong solutions on boiling. This phosphate is fusible.

4. **$(NH_4)_2CO_3$** and **NH_4OH** ppt. from strong solutions white Li_2CO_3, except in presence of much alkali chloride or NH_4Cl.

5. Lithium chloride is soluble in alcohol, ether and amyl alcohol. (Difference from the other alkali chlorides.) On this fact depends the separation of lithium from sodium.

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CHAPTER III.

DETECTION AND SEPARATION OF THE NEGATIVE RADICALS (ANIONS). PRINCIPALLY ACID RADICALS.

DIVISION OF RADICALS INTO GROUPS. (BUNSEN.)

Group I.—Acids whose silver salts are insoluble in water and nitric acid, but whose barium salts are soluble in water. These give a ppt. with $AgNO_3$ in presence of HNO_3, and no ppt. with $BaCl_2$. These are :—Hydrochloric, hydrobromic, hydriodic, hydrocyanic, hydroferricyanic, hydroferrocyanic, thiocyanic and hydrosulphuric (H_2S), and hypochlorous acids.

Group II.—Acids whose silver salts are soluble in nitric acid but not in water, and whose barium salts are soluble in water. These therefore give a ppt. with silver nitrate in *neutral* solutions, and no ppt. with barium chloride. These are :—Nitrous, hypophosphorous, acetic, formic and cyanic acids.

Group III.—Acids whose silver salts are *white*, insoluble in water, soluble in nitric acid, and whose barium salts are insoluble in water, soluble in nitric acid. These give ppts. both with silver nitrate and barium chloride in *neutral* solution. These are :—Sulphurous (selenious and tellurous), phosphorous, carbonic, oxalic, tartaric, citric, iodic, boric, molybdic (selenic and telluric), meta- and pyrophosphoric acids.

Group IV.—Acids whose silver salts are *coloured*, solubility as in III. and whose barium salts are soluble as in III. These are :—Orthophosphoric, arsenious, arsenic, chromic, periodic, thiosulphuric (and vanadic) acids.

Group V.—Acids whose silver and barium salts are both soluble in water and yield no ppt. with either reagent. These are :—Nitric, chloric and perchloric, persulphuric and permanganic acids.

Group VI.—Acids whose silver salts are soluble in water, but whose barium salts are insoluble in nitric acid. They yield a ppt. with barium chloride in presence of nitric acid. These are :—Sulphuric, hydrofluoric and fluosilicic acids.

Group VII. contains non-volatile acids whose only *soluble* salts are those of the alkalis. These are :—Silicic, tungstic, titanic and tantalic acids. (Also several others rarely met with, as zirconic and niobic).

The detection of the acids is divided into

(*a*) Preliminary tests.

(*b*) Confirmatory tests.

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The preliminary tests consist of the treatment of the dry salt with:

(i) **Dilute hydrochloric acid**, with the object of obtaining the free acid if it is volatile, insoluble or unstable, etc. Such acids are:—Carbonic, nitrous, hypochlorous, chloric, sulphurous and thiosulphuric, acetic, cyanic, and some salts of hydrosulphuric (H_2S) and hydrocyanic acids.

(ii) **Strong sulphuric acid**, with the object of obtaining the free acid (or its decomposition products) in cases where the salt is not attacked by dilute hydrochloric acid.

Such acids are:—Hydrofluoric, and *nearly all* salts of hydrochloric, hydrobromic and hydriodic; chloric, perchloric, permanganic, nitric, hydrosulphuric, and the following organic acids:—Ferrocyanic, ferricyanic, hydrocyanic, thiocyanic, formic, acetic, oxalic. Also those acids already mentioned as giving reactions with dilute hydrochloric acid.

(iii) **Salts of non-volatile mineral acids** naturally give no recognisable reaction with either (i) or (ii), *e.g.* phosphoric, boric, sulphuric, arsenic, chromic, molybdic, tungstic, vanadic, etc., also iodic acid.

To carry out the above tests upon a solid salt, one or two grams of the finely powdered salt are placed in a dry test-tube and the reagent added. If nothing happens when cold, heat gently. A gas evolved is tested in the usual ways, or treated with a drop of the required reagent on a glass rod or in the loop of a platinum wire. Or the reagent may be in another test-tube, and the gas allowed to flow in either by gravity or through a delivery tube.

Many substances give off sulphur dioxide when heated with strong sulphuric acid. Such a reaction is *not* conclusive of the presence of a sulphur acid. It is generally due to the action of a reducing agent or the sulphuric acid. This is especially the case with insoluble sulphides, which evolve H_2S in the first instance. This is immediately oxidised by the H_2SO_4 thus:—

$$HgS + H_2SO_4 = HgSO_4 + H_2S$$
$$H_2S + 3H_2SO_4 = 4SO_2 + 4H_2O.$$

REACTIONS OF THE ACID AND NON-METALLIC RADICALS.

GROUP I.

Hydrochloric Acid.

Use dry sodium chloride for 1 *and* 2, *and a solution of it for the rest.*

1. **Dilute HCl.**—No reaction.

2. **Strong H_2SO_4** causes evolution, with effervescence, of colourless HCl gas, which fumes strongly in air (moisture) and reddens blue litmus paper. Some chlorides give the reaction only when heated, and a few give it with difficulty or not at all; these are stannous, mercurous and lead chlorides. The two former yield SO_2 (reducing agents). **Manganese dioxide** mixed with the chloride and treated with strong sulphuric acid causes evolution of chlorine, recognised by its smell and its bleaching action on wet litmus paper. Again, stannous and mercurous chlorides will not give this reaction, but they

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evolve chlorine if powdered potassium bichromate be used instead of manganese dioxide, and the mixture is heated with strong sulphuric acid. (Chromyl chloride [*q.v.*, p. 58] is formed at the same time.)

3. **$AgNO_3$** in neutral solution gives a white ppt. of AgCl, insoluble in dilute nitric acid, soluble in ammonia.

4. **$BaCl_2$** gives no reaction.

N.B—Strong hydrochloric acid, added to $BaCl_2$ solution, gives a crystalline ppt. of $BaCl_2$, an example of the Mass Law as applied to the "solubility product" (see p. 76). This ppt. dissolves on dilution with water.

Hydrobromic Acid, HBr.

Use potassium bromide, solid for 1 *and* 2, *in aqueous solution for remainder.*

1. **Dilute HCl** gives no visible reaction.

2. **Strong H_2SO_4** causes effervescence, with evolution of white fumes of HBr and orange coloured bromine vapour. The production of the free bromine is due to the oxidation of the HBr by the strong sulphuric acid, thus :-

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$

A few bromides require that the mixture be warmed before the above reactions take place. The addition of MnO_2 causes the evolution of bromine more readily. Compare Hg_2Br_2 and $PbBr_2$.

3. **$AgNO_3$** ppts. *very pale* yellow AgBr, insoluble in nitric acid, soluble in ammonia, *but not so readily as the chloride.*

4. **$BaCl_2$** gives no reaction.

5. **Chlorine water** (a very little) added to a *dilute* solution of a bromide sets free bromine. A little CS_2 or chloroform added and shaken up dissolves this bromine, and sinks to the bottom as an orange globule. Excess of chlorine water decolorises the globules owing to the oxidation of the bromine to bromic acid.

$$Br_2 + 5Cl_2 + 6H_2O = 2HBrO_3 + 10HCl.$$

Hydriodic Acid, HI.

Use solid KI for 1 *and* 2, *a solution of it in water for the rest.*

1. **Dilute HCl** gives no reaction.

2. **Strong H_2SO_4** causes effervescence, with evolution of white fumes of HI and violet fumes of free iodine. The iodine is produced by the oxidation of HI by the H_2SO_4. HI is a powerful reducing agent, and part of the H_2SO_4 is reduced to H_2S, which can be smelt, or tested for by a filter paper moistened with lead acetate.

$$2HI + H_2SO_4 = 2H_2O + SO_2 + I_2,$$

also

$$8HI + H_2SO_4 = H_2S + 4H_2O + 4I_2.$$

Note that neither of the iodides of mercury will give this reaction, and lead iodide only on heating.

3. **$AgNO_3$** ppts. yellow AgI, insoluble in nitric acid, almost insoluble in ammonia. It is soluble in KCN and in $Na_2S_2O_3$ solution (photographic reactions).

Silver chloride reacts with soluble iodides, forming AgI.

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4. **Lead acetate or nitrate** ppts. yellow PbI_2, soluble in much hot water to a *colourless* solution, pptg. fine golden scales on cooling.

5. **$CuSO_4$** ppts. white *cuprous* iodide Cu_2I_2 and free iodine, the whole appearing as a brown mixture.

$$2CuSO_4 + 4KI = Cu_2I_2 + K_2SO_4 + I_2.$$

If excess of SO_2 solution be added, the iodine is reduced to HI, and the white Cu_2I_2 is seen.

$$I_2 + 2H_2O + SO_2 = 2HI + H_2SO_4.$$

6. **HNO_2.**—If sodium nitrite be added to an iodide solution and then some dilute HCl (*i.e.* free nitrous acid is formed), iodine is set free (difference from chlorides and bromides).

$$2HNO_2 + 2HI = 2NO + I_2 + 2H_2O.$$

7. **$K_2Cr_2O_7$** in presence of dilute acids sets free iodine from iodides.

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O.$$

8. **Chlorine water** sets free iodine from iodides. Carry out the test as for bromides, No. 5. Excess of chlorine water decolorises the violet globule of iodine in CS_2, owing to the oxidation to HIO_3.

$$I_2 + 5Cl_2 + 6H_2O = 10HCl + 2HI.$$

If a large quantity of iodine is present, some ICl_3 is formed. This gives an orange solution in water, which reacts with ammonia to give a black ppt. of nitrogen iodide of doubtful composition.

Bromine water acts similarly.

Detection of hydrochloric, hydrobromic and hydriodic acids in the presence of one another.

Use a mixture of KCl, KBr and KI.

1. Some of the solid is ground up with some potassium dichromate and warmed gently with strong sulphuric acid. A mixture of the vapours of bromine, iodine and *chromyl chloride* is evolved. If the chromyl chloride be allowed to flow into water in another test-tube, it is converted into chromic acid.

$$4KCl + K_2Cr_2O_7 + 6H_2SO_4 = 6KHSO_4 + 2CrO_2Cl_2 + 3H_2O,$$

and then

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

The chromic acid is tested for in this solution by adding ammonia till alkaline (this destroys free bromine, $2NH_3 + 3Br_2 = 6HBr + N_2$), *acetic* acid till acid and then some *barium* chloride solution. Lemon-yellow barium chromate is obtained.

N.B.—Iodine will mostly condense on the cool parts of the tube in which the reaction is carried out. Lead acetate is not used to test for the chromic acid, because of the chloride which will also be present.

Neither bromides nor iodides give similar reactions to this chromyl chloride test.

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The bromide and iodide are detected as follows :

To some of the very dilute solution is added CS_2 and one drop of chlorine water. Iodides are acted upon first, and on shaking well the CS_2 is coloured violet. *Cautious* addition of chlorine water now decolorises the iodine (see under HI) and then the colour due to bromine appears.

Slight traces of iodide might be missed, if excess of chlorine were contained in one drop of chlorine water. Nitrous acid or potassium dichromate and sulphuric acid may be used instead. These react with iodides, not with bromides. The bromide would be detected with chlorine water afterwards as above.

Another method due to Caven is given as follows (*J. Soc. Chem. Ind.* 1909, **28**, 505)

Acidify the mixed halide solution with dilute sulphuric acid and add sodium nitrite solution. Boil.

Brown solution or black ppt. = iodide. *Cf.* by holding a wet glass rod dipped in starch in the vapour. The starch is coloured purple.	Continue boiling, adding more $NaNO_2$ if necessary, till all iodine is expelled. Neutralise with Na_2CO and evaporate just dry. Add 5 c.cs. of dilute HNO and *just* boil.	
	A brown colour shows bromide. *Cf.* by cooling part of the solution and shaking with CS_2.	Boil rest of solution till all bromide is expelled, adding more dilute HNO_3 to keep up the volume. Add $AgNO_3$. White ppt. soluble in ammonia = chloride.

DETECTION OF FREE HALOGENS.

A. Chlorine.

Detected by smell, by testing with an iodide or bromide as above, or by conversion to chloride by adding excess of ammonia.

$AgNO_3$ reacts thus :

$$3H_2O + 3Cl_2 + 6AgNO_3 = 3AgCl + 3AgClO + 6HNO_3,$$

and after a short time $3AgClO = AgClO_3 + 2AgCl$.

HCl in the presence of chlorine may be detected by shaking with metallic mercury till the smell of chlorine disappears.

$$2Hg + Cl_2 = Hg_2Cl_2.$$

Filter and test the filtrate for HCl.

B. Bromine.

By precisely similar methods as under A for chlorine.

C. Iodine.

Starch solution is coloured blue by free iodine *in the presence of a soluble iodide.* Heat destroys the blue colour.

CS_2 or Chloroform is coloured purple by free iodine.

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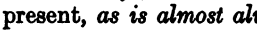
Hypochlorous Acid, HClO.

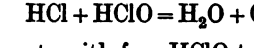
Use bleaching powder, solid or filtered solution, as necessary.

1. **Dilute HCl** is oxidised to chlorine.



$$HClO + HCl = H_2O + Cl_2.$$

2. **Sulphuric acid** sets free hypochlorous acid.



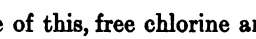
$$NaOCl + H_2SO_4 = NaHSO_4 + HOCl.$$

(Carbonic and nitric act similarly.)

If a chloride is also present, *as is almost always the case*, chlorine is then evolved.

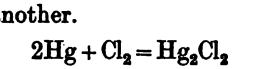
$$HCl + HClO = H_2O + Cl_2.$$

3. **Metallic mercury** reacts with free HClO to form a brown basic mercuric chloride.

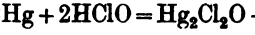


$$2Hg + 2HClO = HgO,\ HgCl_2 + H_2O.$$

By taking advantage of this, free chlorine and free HClO can be detected in the presence of one another.

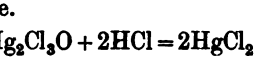


$$2Hg + Cl_2 = Hg_2Cl_2$$



$$2Hg + 2HClO = Hg_2Cl_2O + H_2O.$$

Shake with mercury till no HClO is left, and filter. Treat the ppt. with warm dilute HCl. This dissolves the basic chloride, leaving untouched the white mercurous chloride.



$$Hg_2Cl_3O + 2HCl = 2HgCl_2 + H_2O.$$

Mercury may be detected in the filtrate in the usual way.

Salts of hypochlorous acid react differently with mercury.

Iodide-starch paper is turned blue by hypochlorites in weakly alkaline solutions.

Many metallic hydroxides are acted upon by hypochlorites in *alkaline* solution to form the peroxides (or higher oxides). Difference from chlorates. Thus $Fe(OH)_2$, $Mn(OH)_2$, $Ni(OH)_2$ and $Co(OH)_2$ are so affected. The last named peroxide on warming catalytically decomposes more hypochlorite with evolution of oxygen.

Hydrocyanic (prussic) Acid, HCN.

Use potassium cyanide, KCN.

1. **Dilute HCl** sets free HCN from all soluble cyanides (except mercuric), recognised by its odour of bitter almonds. It is **intensely poisonous**, and is the more dangerous on account of the curious fact that about one person in three is unable to detect it by smell.

2. **Strong H_2SO_4** decomposes *all* cyanides on warming, with evolution of CO.

HCN is the nitrile of formic acid, to which it is hydrolysed by the sulphuric acid.

$HCN + 2H_2O = H.CO.ONH_4$ (ammonium formate). The formic acid, $H.CO.OH$ set free is then decomposed by sulphuric acid in the usual way (see under Formic acid).

$$H.CO.OH - H_2O = CO.$$

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$Hg(CN)_2$ yields CO, CO_2 and SO_2 with hot strong H_2SO_4, owing to its partial decomposition into Hg and C_2N_2 at the temperature of the reaction. The former dissolves in the sulphuric acid in the usual manner.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2, \quad (1)$$

and the cyanogen reacts thus:

$$C_2N_2 + H_2SO_4 + 3H_2O = CO + CO_2 + (NH_4)_2SO_4, \quad (2)$$

adding (1) and (2) we obtain, as the resultant action,

$$Hg(CN)_2 + 3H_2SO_4 + H_2O = HgSO_4 + (NH_4)_2SO_4 + CO + CO_2 + SO_2.$$

3. **$AgNO_3$** added dropwise to a soluble cyanide (except mercuric) gives a white ppt. of AgCN which immediately dissolves in excess of the cyanide.

$$KCN + AgNO_3 = AgCN + KNO_3.$$
$$AgCN + KCN = K[Ag(CN)_2] \text{ (ionised as indicated).}$$

When all the cyanide has been converted into the complex cyanide, further addition of $AgNO_3$ gives a permanent ppt. of AgCN.

$$K[Ag(CN)_2] + AgNO_3 = KNO_3 + 2AgCN.$$

AgCN is insoluble in dilute HNO_3, though somewhat soluble in the strong acid, and soluble in ammonia, thiosulphate and soluble cyanide. It is distinguished from AgCl, etc., which it very much resembles, by its decomposition by strong HCl.

$$HCl + AgCN = HCN + AgCl.$$

When strongly ignited it gives off C_2N_2 and leaves metallic silver.

Very small quantities of cyanide can be detected with certainty by the following reactions.

4. **$Fe(OH)_2$.**—The soluble cyanide is boiled with freshly pptd. ferrous hydroxide obtained by adding a few drops of KOH to a little *freshly made* ferrous sulphate solution.

$$Fe(OH)_2 + 2KCN = Fe(CN)_2 + 2KOH$$
$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6].$$

The solution is then made acid with HCl, and a few drops of $FeCl_3$ then produce a ppt. of prussian blue (ferric ferrocyanide).

(Owing to the presence of ferric iron even in freshly made ferrous sulphate, the blue ppt. is usually obtained on acidifying with HCl.)

5. **$(NH_4)_2S_2$** (*yellow* ammonium sulphide) or other alkaline polysulphide converts a cyanide into a thiocyanate.

$$KCN + (NH_4)_2S_2 = KCNS + (NH_4)_2S.$$

Evaporate to dryness a few drops of each solution in a porcelain basin on the water-bath. Acidify with dilute HCl (to destroy sulphide) and add dilute $FeCl_3$ (one or two drops). The characteristic blood-red $Fe(CNS)_3$ is obtained.

6. **For action of HgO** see under complex cyanides.

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Cyanogen.

When cyanides are heated the actions fall into three classes.

(1) Alkali and alkali earth cyanides melt without decomposition, but will absorb oxygen from air (or from metallic oxides; hence excellent reducing agents).

$$KCN + O = KCNO \text{ (cyanate).}$$

2. Cyanides of noble metals (Ag and Hg) evolve cyanogen gas and leave the metal.

3. Cyanides (simple) of the divalent metals generally evolve N_2 and leave either the metallic carbide or the metal and carbon.

Cyanogen burns with a characteristic "peach blossom" flame, and is excessively poisonous. In some of its reactions it is very like the halogens; thus with alkalis we get a mixture of cyanide and cyanate.

$$2KOH + C_2N_2 = KCN + KCNO + H_2O.$$

The complex cyanogen acids.

Hydroferrocyanic acid $H_4[Fe(CN)_6]$.

Use $K_4[Fe(CN)_6]$.

Dry Tests.

On ignition ferrocyanides yield iron carbide, a cyanide and nitrogen.

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2,$$

thus behaving as a mixture of the two cyanides.

Wet Tests.

1. **Dilute HCl** has no visible action unless boiled, when HCN is evolved.

2. **Strong H_2SO_4** on warming yields CO. (For reactions see under cyanides).

3. **$AgNO_3$** ppts. white $Ag_4Fe(CN)_6$, insoluble in dilute HNO_3 and ammonia; oxidised by strong HNO_3 to silver ferricyanide (reddish-brown), soluble in ammonia.

4. **$BaCl_2$** gives no ppt.

5. **Ferric, ferrous, cupric and uranyl salts** all give characteristic ppts. described under each metal.

Insoluble ferrocyanides, which comprise all except those of the alkalis and alkaline earths, are decomposed by boiling with KOH, diluting, filtering, acidifying the filtrate with HCl, and testing for ferrocyanide. The base is found on the filter, with the exception of zinc, which will dissolve as potassium zincate. It is pptd. by leading in CO_2 and filtering off the insoluble zinc carbonate.

Hydroferricyanic acid, $H_3[Fe^{iii}(CN)_6]$.

Solubility of salts.—All insoluble except those of the alkalis, alkaline earths and the ferric salt.

Use potassium ferricyanide.

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Dry Tests.

On ignition ferricyanides decompose into FeC_2, the cyanide of the base (if stable), cyanogen and nitrogen.

$$2K_3Fe(CN)_6 = 2FeC_2 + 6KCN + C_2N_2 + 2N_2.$$

Wet Tests.

1. **Dilute HCl** evolves HCN *on warming.*
2. **Strong H_2SO_4** decomposes them with evolution of CO.
3. **$AgNO_3$** ppts. orange red $Ag_3Fe(CN)_6$, insoluble in dilute HNO_3, soluble in ammonia.
4. **$BaCl_2$** gives no ppt.
5. **$FeSO_4$** ppts. dark blue ferrous ferricyanide $Fe^{ii}[Fe^{iii}(CN)_6]_2$ (Turnbull's blue).
6. **$FeCl_3$** gives a brown coloration.
7. **$CuSO_4$** ppts. green $Cu_3[Fe(CN)_6]_2$.
8. **KOH.**—In alkaline solutions the acid is a strong oxidising agent, and it is difficult to detect its presence in an insoluble compound. Thus if Turnbull's blue be boiled with potash, the first reaction is

$$Fe_3[Fe(CN)_6]_2 + 6KOH = 2K_3Fe(CN)_6 + 3Fe(OH)_2,$$

but the $Fe(OH)_2$ is oxidised by more ferricyanide,

$$Fe(OH)_2 + KOH + K_3Fe(CN)_6 = K_4Fe(CN)_6 + Fe(OH)_3,$$

and the solution will now contain potassium ferrocyanide.

Alkaline solutions of ferricyanide also oxidise H_2S(pptg. S), HI(pptg. I_2), H_2SO_3 (to H_2SO_4), PbO (to PbO_2) and NH_3 (to N_2).

9. **HgO** (yellow). Almost all cyanides, simple or complex, (excepting $K_3Co(CN)_6$) are completely decomposed by warming the solution with this substance.

$$K_4Fe(CN)_6 + 3HgO + 3H_2O = 4KOH + Fe(OH)_2 + 3Hg(CN)_2.$$

Even insoluble ones, thus:

$$Fe_4[Fe(CN)_6]_3 + 9HgO + 9H_2O = 3Fe(OH)_2 + 4Fe(OH)_3) + 9Hg(CN)_2.$$

This reaction is extremely useful for the separation of metallic cyanides.

Thiocyanic acid, HCNS.

Solubility of salts.—All soluble except those of Ag, Hg, Cu, Au.

Use KCNS.

Dry Tests.

Alkali salts melt readily when heated, undergo colour changes, yellow, brown, green, blue, and become white again on cooling. Those of the heavy metals are completely decomposed, *e.g.*

$$4Cu_2(CNS)_2 = 4Cu_2S + 2CS_2 + 3C_2N_2 + N_2.$$

The mercuric salt is well known as "Pharaoh's serpents' eggs."

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Wet Tests.

1. **Dilute HCl.**—No action.

2. **Fairly strong H_2SO_4** causes the evolution of COS, a gas which burns with a blue flame similar to that of CO, from which it may be distinguished by the production of SO_2 (smell).

$$KCNS + 2H_2SO_4 + H_2O = KHSO_4 + (NH_4)HSO_4 + COS.$$

3. **Strong H_2SO_4** decomposes thiocyanates with violence and the evolution of various products besides COS.

4. **$AgNO_3$** ppts. white AgCNS, insoluble in HNO_3, soluble in ammonia.

5. **$FeCl_3$** gives a blood-red colour, soluble in ether.

6. **$CuSO_4$** gives first an emerald-green colour, then a black ppt. of $Cu(CNS)_2$. This is reduced by SO_2 to white $Cu_2(CNS)_2$ insoluble in dilute acids.

$$2CuSO_4 + 2H_2O + SO_2 + 2KCNS = Cu_2(SCN)_2 + 2KHSO_4 + H_2SO_4.$$

7. **$Co(NO_3)_2$** gives a blue colour, soluble in a mixture of amyl alcohol and ether.

DETECTION OF CYANIDES IN PRESENCE OF FERRO- OR FERRICYANIDES.

Place the mixture in a basin, and treat with cold dilute HCl, and cover with another basin which has been wetted with yellow ammonium sulphide. After a few minutes the volatile HCN will have produced NH_4CNS in the upper basin. Test for this as under cyanides, No. 5.

Hydrosulphuric Acid, H_2S.

Solubility of sulphides.—Those of the alkalis are soluble in water.

Those of Al, Cr and alkaline earths are hydrolysed by water (the latter not so readily as the former).

The remainder are insoluble in water, those of Fe, Mn and Zn being soluble in dilute acids.

Dry Tests.

Heated in air, all sulphides are oxidised with evolution of SO_2. Heated out of contact with air, most are unchanged; those of As and Hg sublime, and polysulphides (*e.g.* FeS_2) give off S.

Wet Tests.

Use powdered Sb_2S_3 or a solution of Na_2S as required.

1. **Dilute HCl**, especially on warming, causes evolution of H_2S, detected by its smell and by a piece of filter-paper moistened with lead acetate.

A few sulphides yield H_2S thus with difficulty or not at all. Those of Hg, Ag, Cu, Ni and Co may be treated with hot strong HCl; the sulphides of As are not affected by this reagent.

2. **Strong H_2SO_4** gives SO_2 on warming.

$$H_2S + H_2SO_4 = 2H_2O + S + SO_2,$$

and is therefore not characteristic, as so many substances reduce strong H_2SO_4.

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3. **Molten NaOH** reacts with insoluble sulphides giving some Na_2S. Extract the melt with water, filter and test for sulphide by one of the wet tests.

4. **$BaCl_2$**—No ppt.

5. **$AgNO_3$** gives, in *neutral* solutions, black Ag_2S, insoluble in cold dilute HNO_3.

6. **Sodium plumbite** (add excess of NaOH to lead acetate solution) gives a black ppt. of PbS. This is an extremely delicate test, and may be used in conjunction with 3 when an insoluble sulphide is being dealt with.

7. **Metallic Silver** is blackened by H_2S and soluble sulphides.

$$H_2S + 2Ag + O\,(\text{air}) = H_2O + Ag_2S.$$

Reaction slow unless water is present.

8. **Oxidising agents**.—Halogens, chromic and nitric acids, ferric salts, etc., cause a ppt. (generally white) of S.

9. **Sodium nitro-prusside** gives a purple colour with water-soluble sulphides.

ACIDS OF GROUP II.

Nitrous Acid, HNO_2.

Solubility of salts.—All nitrites are soluble in water. $AgNO_2$ *sparingly* so in cold water.

Dry Tests.

Heated on charcoal, nitrites cause deflagration.

Wet Tests.

Use $NaNO_2$.

1. **Dilute HCl.**—Effervescence and red-brown fumes of N_2O_3, solution turning pale-blue.

$$2NaNO_2 + 2HCl = 2NaCl + 2HNO_2 \rightarrow H_2O + N_2O_3 \rightarrow NO + NO_2.$$

2. **Strong H_2SO_4** gives somewhat similar reaction, but the gases are readily soluble in the acid.

$$N_2O_3 + 2H_2SO_4 = H_2O + \underset{\text{nitrosyl-sulphuric acid.}}{2H(NO)SO_4}.$$

3. **$AgNO_2$** gives in *neutral* solution a white ppt. of $AgNO_2$ soluble in dilute HNO_3 with evolution of N_2O_3.

4. **$BaCl_2$**.—No reaction.

5. **$FeSO_4$**.—If the reagent contains any free acid, the whole solution turns black, due to the formation of $FeSO_4 . NO$. If the reagent is neutral (which is rarely the case, owing to hydrolysis) the black colour is at once produced by the addition of *dilute* acid, even acetic (*cf.* nitrates).

6. **KI** followed by any acid gives a ppt. of iodine (or a brown coloration)

$$2KI + 2HNO_2 = 2KOH + I_2 + 2NO.$$

Note that here the nitrous acid acts as an *oxidiser*.

7. **Indigo solution** is decolorised by warming with nitrous acid.

8. **$KMnO_4$** in acid solution oxidises nitrous acid to nitric.

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5HNO_3 + 3H_2O.$$

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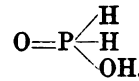
9. ***m*-Phenylene-diamine** in acid solution gives a brown colour (due to formation of Bismarck brown). (P. Griess.)

10. **Brucine** dissolved in strong H_2SO_4 gives no reaction with nitrites (*cf.* nitrates).

Hypophosphorous Acid, H_3PO_2.

All salts are soluble in water. The acid is *monobasic* only, being therefore constituted



Dry Tests.

Ignition causes loss of PH_3 (smell) and formation of phosphate.

$$2H_3PO_2 = PH_3 + H_3PO_4.$$
$$4NaH_2PO_2 = 2PH_3 + H_2O + Na_4P_2O_7.$$

Wet Tests.

1. **Dilute HCl.**—No reaction.
2. **Strong H_2SO_4** is reduced to SO_2 in warming.
3. **$AgNO_3$** is reduced to metallic Ag.

$$NaH_2PO_2 + 4AgNO_3 + 2H_2O = H_3PO_4 + NaNO_3 + 4Ag + 3HNO_3$$

or $$2NaH_2PO_2 + 2AgNO_3 + 4H_2O = 2H_3PO_4 + 2NaNO_3 + 2Ag + 3H_2,$$

according to relative amounts of each present.

4. **$BaCl_2$.**—No reaction.
5. **Salts of some metals, as Cu, Hg, Au,** are reduced to metal.
6. **Strong KOH.**—On heating oxidises them to phosphates with evolution of hydrogen.

$$KH_2PO_2 + 2KOH = 2H_2 + K_3PO_4.$$

Acetic Acid, $CH_3CO.OH$.

Salts are all soluble: the silver salt sparingly.

Use sodium acetate.

Dry Tests.

1. Heated alone, acetone and combustible vapours are evolved and a carbonate (or oxide according to circumstances) is left. Silver acetate leaves the metal.

$$Ca(CH_3CO_2)_2 = (CH_3)_2CO + CaCO_3.$$

2. Heated with NaOH (soda lime) CH_4 is evolved, and sodium carbonate is left.

$$NaOH + CH_3CO_2Na = CH_4 + Na_2CO_3.$$

3. **As_2O_3** mixed with a dry alkali acetate and heated forms *very poisonous* and evil-smelling cacodyl.

$$4Na(CH_3CO_2) + As_2O_3 = Na_2CO_3 + (CH_3)_2As.O.As(CH_3)_2.$$

The reaction is sensitive, but other fatty acids similar to acetic give a similar reaction.

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WET TESTS.

1. **Dilute HCl** sets free acetic acid, detected by smell, especially when gently warmed.

2. **Strong H_2SO_4** gives a similar reaction. If to the mixture one drop of amyl alcohol be added, the characteristic smell (Jargonelle pear-drops) of amyl acetate is obtained.

3. **$AgNO_3$** in *strong neutral* solutions gives a white crystalline ppt. of silver acetate.

4. **$FeCl_3$** gives in neutral solution a red-brown colour, due to ferric acetate. On boiling this is hydrolysed, and a brown basic ferric acetate is pptd. (quantitatively if sufficiently diluted).

$$Fe(CH_3CO_2)_3 + 2H.OH = Fe(OH)_2(CH_3CO_2) + 2H_4C_2O_2.$$

Formic Acid, H.CO.OH.

All formates are soluble, those of Ag and Pb sparingly. *Use sodium formate, solid or solution as required.*

DRY TESTS.

When heated formates give off inflammable vapours and leave a residue of carbonate (oxide or metal).

WET TESTS.

1. **Dilute HCl.**—No visible reaction, but the smell of formic acid is apparent on warming gently.

2. **Strong H_2SO_4** evolves CO, due to the dehydration of formic acid. The CO is recognised by its characteristic blue flame when burning.

$$H_2CO_2 = CO + H_2O.$$

3. **$AgNO_3$** in neutral solution, gives a white ppt. of silver formate, which rapidly becomes black, especially on warming. Formic acid (formed by hydrolysis) is a powerful reducing agent.

$$4Ag(CHO_2) + 2H_2O = 4Ag + 2H_2O + 2CO_2.$$

4. **$FeCl_3$** in neutral solution gives reactions precisely similar to those given by acetates.

Cyanic Acid, HCNO.

Salts of alkalis and alkali earths are soluble in water. The cyanates are stable to heat, being formed when cyanides are fused with oxidising agents (or even in air).

Use potassium cyanate.

WET TESTS.

1. **Dilute HCl** gives off CO_2, caused by the immediate decomposition of the cyanic acid set free.

$$HCNO + H_2O = CO_2 + NH_3.$$

Small amounts of HCNO are also given off, recognisable by its penetrating smell.

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2. **Strong H_2SO_4** acts similarly.
3. **$AgNO_3$** in neutral solution ppts. white AgCNO soluble in dilute HNO_3.
4. **Cobalt Acetate** gives a blue colour with soluble cyanates.

(1) $$Co(CH_3CO_2)_2 + 2KCNO = Co(CNO)_2 + 2K(CH_3CO_2).$$

(2) $$2KCNO + Co(CNO)_2 = \underset{\text{blue.}}{K_2[Co(CNO)_4]}.$$

If largely diluted with water, reaction (2) goes backwards and the blue colour disappears. This reaction may be used to detect KCNO in KCN. The cyanide must first be destroyed by bubbling CO_2 through the solution for several hours.

$$KCN + H_2CO_3 = HCN \uparrow + KHCO_3.$$

Add alcohol, filter from pptd. $KHCO_3$ and add cobalt acetate to the filtrate (Schneider).

ACIDS OF GROUP III.

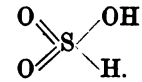
$AgNO_3$ gives a white ppt. soluble in nitric acid. $BaCl_2$ does the same.

Sulphurous Acid, H_2SO_3.

Free acid unknown except in solution.

This acid is **tautomeric**, appearing sometimes to be constituted

and sometimes



Solubility of salts.—The alkali salts are soluble in water, the remainder either very slightly so or insoluble. All easily soluble in dilute hydrochloric acid.

Use sodium sulphite, solid or solution in water, as required.

Dry Tests.

On ignition out of contact with air, all sulphites except those of the alkalis give off SO_2 and leave the metallic oxide.

$$ZnSO_3 = ZnO + SO_2,$$

or the metal and oxygen if the oxide is unstable.

$$Ag_2SO_3 = 2Ag + SO_2 + O$$

(*cf.* carbonates).

Alkali sulphites are partly oxidised to sulphates at the expense of the other part, which is reduced to sulphide.

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S.$$

A very high temperature for some time is necessary to complete the reaction (*cf.* thiosulphates).

Wet Tests.

1. **Dilute HCl** gives off SO_2 in the cold, recognised by its odour.

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2.$$

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2. **Strong H_2SO_4** reacts similarly, but more vigorously.

3. **$AgNO_3$** ppts. white Ag_2SO_3 from *neutral* solutions, soluble in nitric acid and in alkali sulphites.

$$Ag_2SO_3 + Na_2SO_3 = 2AgNaSO_3.$$

By boiling this solution a grey ppt. of silver is formed.

$$2AgNaSO_3 = 2Ag + Na_2SO_4 + SO_2.$$

If the ppt. of Ag_2SO_3 suspended in *water* is boiled the reaction is different.

$$2Ag_2SO_3 = Ag_2SO_4 + SO_2 + 2Ag.$$

4. **$BaCl_2$** ppts. white $BaSO_3$ from neutral solutions (not from sulphurous acid itself) soluble in dilute HNO_3. As, however, most sulphites contain sulphates, the ppt. will not usually dissolve completely. Ordinary sodium sulphite usually contains much sodium sulphate.

Strontium chloride behaves similarly. (See thiosulphuric acid).

5. **Iodine solution** is decolorised by sulphurous acid

$$H_2SO_3 + O\ H_2 + I_2 = H_2SO_4 + 2HI.$$

This reaction is used in estimating sulphurous acid.

6. **Acid permanganate solution** oxidises sulphurous acid, but the reaction varies according to conditions, sulphuric and dithionic acids being formed.

7. **$K_2Cr_2O_7$** in acid solution is reduced to the green chromic salt

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

8. Sulphurous acid also reduces mercuric chloride (boiling), mercurous nitrate and gold salts.

Phosphorous Acid, H_3PO_3.

Dibasic. Constitution therefore $O{=}P\begin{cases}OH\\OH\\H.\end{cases}$

Solubility of salts.—Only alkali salts soluble in water, but all soluble in dilute acid.

Use sodium phosphite, solid or solution as required.

Dry Tests.

By ignition, both the free acid and the phosphites are partly oxidised at the expense of the other part.

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$
$$8Na_2HPO_4 = 4Na_3PO_4 + Na_4P_2O_7 + 2PH_3 + H_2O.$$

The PH_3 is recognised by its smell and inflammability.

Wet Tests.

1. **Dilute HCl.**—No visible action.

2. **Strong H_2SO_4** is reduced, on warming, to SO_2.

$$H_3PO_3 + H_2SO_4 = H_3PO_4 + SO_2 + H_2O.$$

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3. **$AgNO_3$** ppts. white Ag_2HPO_3 from neutral solutions. This in strong solutions is at once reduced to metallic Ag : in dilute solution only on warming,

$$Ag_2HPO_3 + H_2O = H_3PO_4 + 2Ag.$$

4. **$BaCl_2$** ppts. white $BaHPO_3$, soluble in acids.

5. **$HgCl_2$** is reduced to Hg_2Cl_2, slowly in the cold, rapidly on warming, by free H_3PO_3.

$$2HgCl_2 + H_3PO_3 + H_2O = Hg_2Cl_2 + 2HCl + H_3PO_4.$$

In *hot* solution excess of H_3PO_3 causes further reduction to mercury in a similar manner.

6. **Strong KOHaq** oxidises phosphites to phosphates.

$$K_2HPO_3 + KOH = K_3PO_4 + H_2.$$

Carbonic Acid, H_2CO_3.

Free acid quite unknown except in dilute solution.

Solubility of salts.—Alkali carbonates only are soluble in water. All carbonates are soluble in dilute acids : $MgCO_3$ (native) dissolves only in *hot* dilute acids. Many carbonates readily form bicarbonates with excess of carbonic acid, all of which are soluble in water and decomposed again by boiling.

Dry Tests.

All carbonates except those of the alkalis are decomposed by heat.

$$CaCO_3 = CaO + CO_2.$$

The carbonates of Ca, Sr and Ba require a very high temperature : $BaCO_3$ is not completely decomposed by heat alone. (See p. 10.)

Wet Tests.

1. **Dilute HCl** causes evolution of CO_2 from all carbonates. ($MgCO_3$ requires to be heated.)

2. **Strong H_2SO_4** does the same.

3. **$AgNO_3$** ppts. white Ag_2CO_3 from *neutral* carbonate solutions. Boiling converts it into a yellow basic carbonate.

4. **$BaCl_2$** ppts. white $BaCO_3$ from *neutral* solutions.

5. **Litmus** is turned blue by alkali carbonates. Alkali bicarbonates are practically neutral to litmus and phenolphthaleïn.

Methyl orange is unaffected by free carbonic acid, alkali carbonates and bicarbonates reacting alkaline to it.

Oxalic Acid, $H_2C_2O_4$, $2H_2O$.

The free acid is a white crystalline substance. The salts are insoluble in water except those of the alkalis, but all are soluble in dilute HCl.

Oxalic acid, besides forming ordinary acid salts with monacid bases, forms "quadroxalates," *e.g.* KHC_2O_4, $H_2C_2O_4$, $2H_2O$. "Salts of sorrel."

Dry Tests.

The free acid, on ignition, gives off water of crystallisation and sublimes, with partial decomposition, into a snow-white solid, the anhydrous acid.

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All oxalates are decomposed by gentle ignition with evolution of CO and formation of carbonates. The oxalates of the noble metals therefore, of course, leave the metal itself, and so also do those of nickel, cobalt and copper (out of contact with air).

$$CuC_2O_4 = Cu + 2CO_2.$$

Wet Tests.

Use a solution of ammonium oxalate.

1. **Dilute HCl** (on the solid) no visible reaction.
2. **Strong H_2SO_4** (on the solid) evolves CO and CO_2 by dehydrating the acid.

$$H_2C_2O_4 - H_2O = CO + CO_2.$$

Test for CO_2 *first*, for obvious reasons.

3. **$AgNO_3$** ppts. white $Ag_2C_2O_4$ from neutral solutions.
4. **$BaCl_2$** ppts. white BaC_2O_4.
5. **$CaCl_2$**, which is generally used, ppts. white CaC_2O_4, insoluble in *acetic* acid. This ppt. cannot be filtered if pptd. in the cold, but readily settles when pptd. at the boiling temperature. Washed by decantation, treated with hot dilute H_2SO_4 and then permanganate, the latter is decolorised in a very characteristic way, *q.v.*
6. **$KMnO_4$** in presence of H_2SO_4 is not reduced by oxalates in the cold, but on warming is reduced slowly at first, then more rapidly.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = 10CO_2 + K_2SO_4 + MnSO_4 + 8H_2O.$$

7. **MnO_2** in presence of hot dilute sulphuric acid oxidises oxalic acid to CO_2.

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

Tartaric Acid, $H_2(C_4H_4O_6)$.

Constitution: COOH-CHOH-CHOH-COOH.

Clear crystals (monoclinic), no water of crystallisation.

Solubility of salts.—Neutral alkali salts very soluble in water, so is the acid sodium salt, but the acid potassium and ammonium salts dissolve with difficulty in cold water.

All others dissolve with difficulty in water, but readily in alkali tartrates, forming complex salts.

Dry Tests.

Tartaric acid melts at 135°C. On ignition it is decomposed with evolution of various gases and smell of burnt sugar. A residue of carbon is left.

Alkali tartrates behave similarly, but leave a residue of carbon and alkali carbonate (ammonium tartrate residue is carbon only).

Alkaline earth tartrates leave a residue of carbon and carbonate which by ignition is changed to oxide. Tartrates of metals whose oxides are reducible by carbon leave a metallic residue.

Wet Tests.

Use Rochelle salt, $KNa(C_4H_4O_6)$, solid or in solution as required.

1. **Dilute HCl.**—No action.

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2. **Strong H_2SO_4** causes carbonisation on warming, and evolution of CO_2 and SO_2.

3. **$AgNO_3$** in *neutral* solutions gives a white ppt. of $Ag_2C_4H_4O_6$ soluble in acids and in ammonia. When the ammoniacal solution is heated a mirror of silver is deposited on the tube. Carry out thus:

The *pure* tartrate solution is treated with $AgNO_3$ (not too dilute) and then very dilute ammonia added dropwise till the ppt. has nearly, but not quite dissolved. On heating to 100° in boiling water a mirror is gradually deposited; more quickly on boiling. As other acids interfere with this test, the tartaric acid should be pptd. as $KHC_4H_4O_6$ by treating the solution with solid K_2CO_3 till alkaline and then adding acetic acid. Filter, wash and dissolve in KOHaq (the absolute minimum).

4. **$BaCl_2$ and $CaCl_2$** (latter generally used).—In *neutral* solution ppts. white calcium tartrate, readily soluble in alkali tartrate to form a double salt. After addition of sufficient $CaCl_2$ to decompose this a permanent ppt. is obtained.

$$2K_2C_4H_4O_6 + CaCl_2 = 2KCl + \underset{\text{(soluble)}}{K_2Ca(C_4H_4O_6)_2}.$$

$$K_2Ca(C_4H_4O_6)_2 + CaCl_2 = 2KCl + 2Ca(C_4H_4O_6).$$

The presence of ammonium salts hinders the reaction, but does not prevent it (*cf.* citrates). Calcium tartrate is soluble in acetic acid and in KOH (*cf.* oxalate).

5. **KCl** added to a strong *neutral* tartrate solution and acidified with acetic acid ppts. $KHC_4H_4O_6$.

6. **Alkaline $KMnO_4$** is reduced on heating first to green manganate and then rapidly to $MnO(OH)_2$.

Citric Acid, $H_3(C_6H_5O_7)$.

Constitution: $C\begin{cases} CH_2 . COOH \\ OH \\ COOH \\ CH_2 . COOH. \end{cases}$

Solubility of salts.—Alkali citrates are soluble in water and readily form soluble double citrates with citrates of heavy metals.

Dry Tests.

Somewhat similar to tartrates. The smell, however, is less like that of burnt sugar.

Wet Tests.

Use potassium citrate, $K_3(C_6H_5O_7)$.

1. **Dilute HCl.**—No visible action.

2. **Strong H_2SO_4** on warming causes charring and evolution of CO_2, SO_2, etc., but less readily than with tartrates. *Cf.* both at 100°.

3. **$AgNO_3$** ppts. white $Ag_3(C_6H_5O_7)$ from neutral solutions. No silver mirror is formed by heating the ammoniacal solution to 100°, but on continued boiling some silver is deposited.

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4. **$BaCl_2$ and $CaCl_2$** (latter generally used).—No ppt. in neutral solution, but as calcium citrate is more soluble in cold water than in hot, a ppt. is obtained on heating the solution.

Ammonium salts hinder somewhat.

5. **$Ca(OH)_2aq$** causes no ppt. in cold neutral solutions, but on boiling a ppt. is formed which redissolves on cooling. *Cf.* 4, in which the calcium citrate obtained on boiling does *not* redissolve on cooling: it forms a heavy crystalline ppt. different (polymer) from the flocculent ppt. formed at first.

6. **Alkaline $KMnO_4$** on warming is reduced to green manganate only (except by prolonged boiling). Difference from tartrates.

Iodic Acid, HIO_3.

Solubility.—Alkali salts soluble in water. Remainder difficultly soluble or insoluble.

Dry Tests.

Heated on charcoal, moderate deflagration occurs. Heated alone, all iodates decompose into iodide and oxygen. The free acid of the "bi-iodates," *e.g.* KIO_3, HIO_3, yields free iodine also. $2HIO_3 = H_2O + 5O + I_2$.

Wet Tests.

Use potassium iodate, KIO_3.

1. **Dilute HCl.**—No action.

2. **Strong H_2SO_4.**—No action unless reducing substances are present also, when iodine is separated, *e.g.*

$$KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3I_2.$$

3. **$AgNO_3$** ppts. white $AgIO_3$ not *easily* soluble in HNO_3, soluble in ammonia.

4. **$BaCl_2$** ppts. white $Ba(IO_3)_2$, difficultly soluble even in hot water.

5. **H_2SO_3** causes separation of iodine (unless a large excess is used), thus:

(*a*) $$KIO_3 + 3H_2SO_3 = KI + 3H_2SO_4.$$

(*b*) $$KI + H_2SO_4 = KHSO_4 + HI.$$

$$KIO_3 + H_2SO_4 = KHSO_4 + HIO_3.$$

and then (*c*) $$5HI + HIO_3 = 3H_2O + 3I_2.$$

If, however, too much H_2SO_3 is added,

$$2H_2O + SO_2 + I_2 = 2HI + H_2SO_4.$$

Boric Acid, H_3BO_3.

Solubility of salts.—Alkali borates soluble in water, giving a strongly alkaline solution (hydrolysis). Remainder not soluble in water, but in dilute acids and in NH_4Claq.

All the salts are derived from either the meta- or pyro-acid, HBO_2 or $H_2B_4O_7$.

Dry Tests.

Alkali borates melt to a colourless glass with effervescence (water of crystallisation), when heated alone or on charcoal. Remainder unaffected.

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Wet Tests.

Use borax, $Na_2B_4O_7$, $10H_2O$.

1. **Dilute HCl.**—No visible action.

2. **Strong H_2SO_4.**—No visible action. The boric acid set free, however, can colour the flame a characteristic green. This can be seen by holding some of the mixture *close to* but not *in* a bunsen flame.

3. **Alcohols** (especially methyl) *readily* form the ester, which burns with a green-mantled flame. Mix borax to a paste with strong H_2SO_4 in a basin, add methylated spirit and set alight.

4. **$AgNO_3$** in strong solutions ppts. white $AgBO_2$, which is hydrolysed to Ag_2O on warming. If the borax solution is sufficiently dilute Ag_2O is pptd. in the cold, owing to the complete hydrolysis of the borate.

5. **$BaCl_2$** ppts. white $Ba(BO_2)_2$ from not too dilute solutions, soluble in excess of $BaCl_2$ and in NH_4Cl.

6. **Turmeric.**—A piece of turmeric paper moistened with *free* boric acid (borate and dilute HCl) and *then dried*, is coloured reddish-brown. If this colour is moistened with KOH it becomes greenish-black.

Molybdic Acid, H_2MoO_4.

Solubility of salts.—Those of alkalis soluble in water, remainder only in acids.

The most important salts are the acid ammonium molybdate of commerce, $(NH_4)_6Mo_7O_{24}$, $4H_2O$, and the minerals wulfenite, $PbMoO_4$, and powellite, $CaMoO_4$.

Dry Tests.

Alkali molybdates are reducible on charcoal to grey metallic molybdenum, with a white incrustation of MoO_3.

The borax bead is coloured yellow when hot, colourless when cold, in oxidising flame; turbid brown in the reducing flame.

Wet Tests.

Use ammonium molybdate dissolved in water.

1. **Dilute HCl** on the *solution* ppts. white H_2MoO_4, soluble in excess of acid.

2. **Strong H_2SO_4.**—Evaporate a few drops of the molybdate solution with a drop of the reagent in a porcelain basin. An intense blue mass is obtained.

3. **$AgNO_3$** ppts. white silver molybdate, soluble in nitric acid and in ammonia.

4. **$BaCl_2$** ppts. white $BaMoO_4$, soluble in HNO_3.

5. **H_2S** colours molybdenum solutions blue and then gradually ppts. MoS_3, soluble in ammonium sulphide.

6. **Zn.**—A molybdate solution made acid with sulphuric acid and treated with zinc turns first blue, then green, finally brown. $SnCl_2$, etc., cause the same reaction. (Reduction products of MoO_3.)

7. **Na_2HPO_4** added to excess of an ammonium molybdate solution strongly acid with HNO_3 and warmed gently, ppts. canary-yellow ammonium phosphomolybdate.

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CHEMISTRY DEPARTMENT California College of Pharmacy

Meta-Phosphoric Acid, HPO_3.

$NaPO_3$ is obtained by igniting microcosmic salt.

$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O.$$

Solubility of salts.—Alkali salts soluble in water. Remainder insoluble in water, soluble in mineral acids, metaphosphoric acid or alkali metaphosphates.

DRY TESTS.

On fusion the alkali salts form a glassy mass similar to a borax bead, which similarly dissolves many metallic oxides.

WET TESTS.

Use sodium metaphosphate (from microcosmic salt).

1. **Dilute HCl and strong H_2SO_4.**—No visible action.
2. **$AgNO_3$** ppts. white $AgPO_3$ from neutral solutions soluble in HNO_3 and in ammonia.
3. **$BaCl_2$** ppts. white bulky $Ba(PO_3)_2$, soluble in excess of the metaphosphate.
4. **Ammonium molybdate and HNO_3** cause no ppt. in cold; on boiling the meta- becomes ortho-phosphate and the yellow ppt. of ammonium phosphomolybdate appears.

$$NaPO_3 + H_2O = NaH_2PO_4.$$

5. **Albumen** solution is coagulated by the *free acid* (*cf.* pyro- and ortho-acids). To obtain the free acid from a metaphosphate acidify with *acetic* acid.

Pyro-Phosphoric Acid, $H_4P_2O_7$.

Salts are obtained by igniting monacid salts of the orthoacid.

$$Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

Solubility of salts.—Alkali salts soluble in water. Remainder in dilute acids.

DRY TESTS.

None in particular. The salts are not readily fusible.

WET TESTS.

Use sodium pyro-phosphate made as above.

1. **HCl and H_2SO_4.**—No visible action.
2. **$AgNO_3$** ppts. white $Ag_4P_2O_7$, soluble in HNO_3 and in ammonia.
3. **$BaCl_2$** ppts. white $Ba_2P_2O_7$, soluble in acids.
4. **Ammonium molybdate.**—Same as meta-phosphate.
5. **Albumen** is *not* coagulated by the free acid.

GROUP IV.

$AgNO_3$ gives a *coloured* ppt. soluble in HNO_3 and in ammonia.
$BaCl_2$ gives a ppt. soluble in HNO_3.

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Ortho-Phosphoric Acid, H_3PO_4.

Solubility of salts.—All the alkali salts are soluble in water; so are the primary salts of the alkaline earths ("super-phosphate") $Ca(H_2PO_4)_2$. Remainder difficultly soluble or insoluble. All soluble in dilute mineral acids and all except lead, ferric, chromic and aluminium phosphates soluble in acetic.

Dry Tests.

On ignition:

The alkali tertiary salts melt without decomposition.

The secondary salts change to pyrophosphate.

$$Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

The primary salts *and* microcosmic salt change to metaphosphate.

$$NaH_2PO_4 = NaPO_3 + N_2O.$$

Wet Tests.

1. **HCl or H_2SO_4.**—No visible reaction.

2. **$AgNO_3$** in neutral solutions ppts. pale yellow Ag_3PO_4 (Difference from meta- and pyro-acids), soluble in HNO_3 and in ammonia.

3. **$BaCl_2$** ppts. white $Ba_3(PO_4)_2$, soluble in acids.

4. **Magnesia mixture** ($[NH_4]_2MgCl_4 + NH_4OH$) ppts. white crystalline $MgNH_4PO_4$, $6H_2O$, insoluble in dilute ammonia. This ppt. should be examined under a microscope ($\frac{1}{6}$ in. objective). It is very characteristic (*cf.* arsenic acid).

5. **$FeCl_3$** ppts. pale yellow $FePO_4$, quantitatively in the presence of sodium acetate (which replaces the HCl formed by acetic acid).

$$Na_2HPO_4 + CH_3CO_2Na + FeCl_3 = 3NaCl + CH_3CO_2H + FePO_4.$$

Advantage of this is taken in the separation of phosphoric acid from the bases (Group III. C).

6. **Ammonium molybdate** in excess, in the presence of much nitric acid, ppts. (slowly cold, rapidly on warming) yellow ammonium phospho-molybdate, soluble in ammonia, insoluble in nitric acid. Much HCl will considerably hinder the pptn. as will the presence of an oxalate.

The yellow ppt. has the composition $(NH_4)_3PO_4 + 12MoO_3$.

7. **Metastannic acid** ($Sn + HNO_3$) forms an insoluble phosphostannic acid (?), and is used to separate phosphoric acid from the metals.

Chromic, arsenic and arsenious acids have already been described.

Thiosulphuric Acid, $H_2S_2O_3$.

Constitution $SO_2(SH)(OH)$.

Free acid unknown, owing to its instability.

Solubility of salts.—Alkali salts soluble in water. Remainder difficultly so, but many are soluble in sodium (etc.) thiosulphate, forming complexes.

Dry Tests.

On ignition away from air the alkali thiosulphates yield a mixture of sulphate and sulphide and a sublimate of sulphur. The ignition must be

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prolonged and at a high temperature for the completion of the reaction. (*Cf.* sulphites.) $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S + 4S$.

Wet Tests.

Use sodium thiosulphate, $Na_2S_2O_3$, $5H_2O$.

1. **Dilute HCl** causes deposition of sulphur and evolution of SO_2.

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 + S.$$

If the acid is added to a very dilute solution of the thiosulphate, the reaction takes place slowly: apparently due to the slower pptn. of colloidal sulphur.

2. **Strong H_2SO_4** as in 1, but more violently.

3. **$AgNO_3$** ppts. white $Ag_2S_2O_3$, which turns yellow, brown and black, especially on warming.

$$Ag_2S_2O_3 + H_2O = H_2SO_4 + Ag_2S.$$

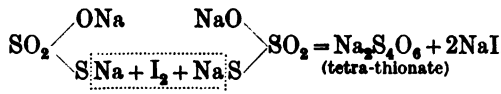
$Ag_2S_2O_3$ is soluble in excess of thiosulphate, forming a complex salt $Na_4[Ag_2(S_2O_3)_3]$, this is decomposed by boiling, giving a ppt. of Ag_2S.

$$Na_4[Ag_2(S_2O_3)_3] = Ag_2S + Na_2SO_4 + Na_2S_2O_3 + SO_2 + S.$$

(*Cf.* copper.)

4. **$BaCl_2$** in not too dilute a solution ppts. white crystalline BaS_2O_3.

5. **Iodine** solution (in KI) is decolorised.



Chlorine and bromine act quite differently.

$$Na_2S_2O_3 + H_2O + Cl_2 = 2NaCl + S + H_2SO_4,$$

and then, if sufficient chlorine be used:

$$S + 3Cl_2 + 4H_2O = 6HCl + H_2SO_4.$$

6. **$FeCl_3$** gives a violet colour (ferric thiosulphate) which soon disappears.

$$FeCl_3 + 2Na_2S_2O_3 = 2NaCl + 2FeCl_2 + Na_2S_4O_6.$$

(*Weak oxidising agent, cf. iodine.*)

7. **$CuSO_4$** similarly oxidises it to $Na_2S_4O_6$ with production of sodium cupr*ous* thiosulphate, $Na_2[Cu_2(S_2O_3)_2]$, which on acidifying and boiling ppts. Cu_2S. Hence useful separation of copper from cadmium.

GROUP V.

$AgNO_3$ gives NO ppt.
$BaCl_2$ gives NO ppt.

Nitric Acid, HNO_3.

All nitrates are soluble in water, except *basic* ones.

Dry Tests.

Heated on charcoal, nitrates cause deflagration. On ignition, the alkali nitrates evolve oxygen and leave a nitrite; ammonium nitrate is decomposed

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into nitrous oxide, N_2O, and water, and the remaining nitrates are decomposed into the metallic oxide (or metal) NO_2 and oxygen.

(1) $KNO_3 = KNO_2 + O.$

(2) $NH_4NO_3 = N_2O + 2H_2O.$

(3) $Pb(NO_3)_2 = PbO + 2NO_2 + O.$

(4) $2AgNO_3 = Ag_2 + 2NO_2 + O_2.$

Wet Tests.

Use KNO_3.

1. **Dilute HCl.**—No reaction.

2. **Strong H_2SO_4** on warming causes evolution of nitric acid, appearing as white and faint brown fumes, condensing on the cool portion of the tube to a liquid which runs down in characteristic streaks.

3. **$AgNO_3$ and $BaCl_2$.**—No reactions.

4. **$FeSO_4$** is oxidised by nitric acid as follows :

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

The NO dissolves in excess of ferrous sulphate, forming a black solution, $FeSO_4 . NO$.

The test is carried out thus :

To a little of the nitrate solution add cold strong ferrous sulphate solution and pour strong sulphuric acid down the side of the tube so that it forms a separate layer at the bottom. A black ring is formed at the junction of the two layers.

N.B.—If a bromide or iodide be present, a ring somewhat similar in appearance, consisting of bromine or iodine, will be formed. This ring, of course, would be formed in the absence of ferrous sulphate. In case of such a mixture the halogen is removed by pptn. with silver *sulphate* and the filtrate tested for nitrate.

5. Several **organic reagents** are now employed both for detection and estimation of nitric acid. The most important are :

(*a*) **Diphenylamine** (·1 gm. in 20 c.cs. of pure H_2SO_4 and 4 c.cs. of water).—Stratify the solutions. A blue ring appears at the contact zone.

(*N.B.*—This reaction is also caused by other oxidising agents.)

(*b*) **Brucine** (·2 gms. in 100 c.cs. of H_2SO_4).—Mix solution to be tested with excess of strong sulphuric acid and add a little of the brucine solution. A red colour appears, changing to orange, yellow and finally greenish.

(*c*) "**Nitron**" (diphenylene-dianilo-dihydro-triazole). This base dissolved in dilute acetic acid gives a colourless crystalline ppt. (will detect 1 in 60,000).

6. **Zn dust and KOH** reduces nitrates to ammonia and is used to detect nitrates in the presence of chlorates, etc., which oxidise the ferrous sulphate. Nitrites give the same reaction.

Chloric Acid, $HClO_3$.

The free acid is dangerously unstable, and is unlikely to be met with except in dilute solution.

Solubility.—All chlorates are soluble in water.

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Dry Tests.

Heated on charcoal, chlorates cause violent deflagration. Heated alone, all evolve oxygen and leave a chloride.

Wet Tests.

Use potassium chlorate, $KClO_3$.

1. **Dilute HCl.**—No action in the cold. On warming slight evolution of chlorine usually occurs. With strong HCl a violent evolution of gas takes place.

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 9Cl + \underset{\text{"euchlorine"}}{3ClO_2}.$$

2. **Strong H_2SO_4.**—The mixture turns yellow, and on warming violent explosions occur. *Hence use a very small quantity of chlorate for this test.*

The explosions are due to the breaking up of free chloric acid, thus :

$$3HClO_3 = HClO_4 + H_2O + ClO_2 \text{ (yellow)}$$

and also $$2ClO_2 = Cl_2 + 2O_2.$$

3. **$AgNO_3$ and $BaCl_2$.**—Neither cause any reaction.

4. **Nascent hydrogen** (from zinc and acid or alkali) reduces chlorates to chlorides.

5. **Ferrous salts** are oxidised to ferric salts by *boiling* with a chlorate and dilute sulphuric acid.

Perchloric Acid, $HClO_4$.

This acid is now sold as a reagent for potassium.

Solubility.—All perchlorates are soluble in water.

Use $KClO_4$, except for No. 5, for which use the acid.

Dry Tests.

Heated on charcoal, deflagration takes place. Heated alone, oxygen is evolved, though less readily than from chlorates, and a chloride is left.

Wet Tests.

1. **HCl** dilute or strong causes no reaction (*cf.* chlorates).

2. **Strong H_2SO_4** on heating causes evolution of thick white fumes of perchloric acid.

3. **$AgNO_3$ and $BaCl_2$.**—No reaction.

4. **Ferrous salts** are *not* oxidised by perchloric acid. Hence separation from chloric.

5. **KCl (or KNO_3)** solution ppts. white crystalline $KClO_4$ from not very dilute solutions.

6. **Nascent Hydrogen** does *not* reduce perchlorates, nor does SO_2.

Persulphuric Acid, $H_2S_2O_8$.

Ammonium persulphate is much used as an oxidising agent. It is also employed in photography for reducing dense negatives.

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Wet Tests.

1. **Dilute acids**, and even *water* alone, especially on warming, cause decomposition. $K_2S_2O_8 + H_2O = 2KHSO_4 + O$.

Some of the oxygen comes off as ozone, whose smell is unmistakable.

2. **Strong H_2SO_4.**—Mixed with a persulphate at 0°C. forms a strongly oxidising liquid called **Caro's acid**.

3. **$BaCl_2$.**—No reaction in cold, but on standing or warming $BaSO_4$ is pptd. (See 1.)

4. **$AgNO_3$** causes a black ppt. of Ag_2O_2.

$$2H_2O + Ag_2S_2O_8 = Ag_2O_2 + 2H_2SO_4.$$

Note.—No ppt. of $Ag_2S_2O_8$ is obtained; hence the inclusion of this acid in Group V.

5. **Hydroxides of metals** possessing a higher oxide are oxidised to that higher oxide, *e.g.* ferrous, manganous, nickel, cobalt and lead salts. (Add KOH and then the persulphate).

$$Pb(OH)_2 + K_2S_2O_8 + H_2O = 2KHSO_4 + PbO_2 + H_2O.$$

Permanganic acid has been discussed under Manganese.

GROUP VI.

$AgNO_3$.—No reaction.

$BaCl_2$.—Ppt. insoluble in nitric acid.

Sulphuric Acid, H_2SO_4.

Solubility.—All soluble in water except those of lead, barium and strontium. Calcium sulphate is not very soluble in water, but readily in dilute HCl.

Dry Tests.

Sulphates of "heavy" metals when ignited *strongly* partly yield SO_3 and the oxide (or metal if oxide is unstable). Exceptions are the alkali earths and lead.

Heated on charcoal, with fusion mixture, are partly reduced to sulphides, and will give a black stain on a wet silver coin, etc.

Wet Tests.

1. **Dilute HCl.**—No reaction.
2. **Strong H_2SO_4.**—No reaction.
3. **$AgNO_3$.**—No reaction.
4. **$BaCl_2$** ppts. white $BaSO_4$, insoluble in any dilute acid.

Hydrofluoric Acid, HF.

Solubility.—Alkali fluorides and those of Al, Ag, Sn and Hg only are soluble in water. "Acid" salts, *e.g.* KF . HF, are well known.

Fluorides of the alkali earths are fairly soluble in dilute HCl when boiled, but on neutralising the acid they are repptd.

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Dry Tests.

"Acid" fluorides only are affected by ignition, evolving hydrofluoric acid.

Mixed with silica, moistened and heated, they are decomposed thus:

$$CaF_2 + H_2O + SiO_2 = CaSiO_3 + 2HF,$$

or in absence of moisture, and when strongly ignited:

$$6CaF_2 + 6SiO_2 = 2CaSiF_6 + 4CaSiO_3 \text{ (incompletely fluosilicate).}$$

Wet Tests.

1. **Dilute HCl.**—No reaction.

2. **Strong H_2SO_4** on gently heating evolves HF, a fuming gas which etches glass. This test is carried out by mixing the fluoride to a paste with the acid in a lead (or platinum) crucible, and covering with a watch-glass whose under surface has been thinly covered with paraffin wax and a device scratched in it with a pin. The watch-glass is filled with cold water and the basin cautiously warmed (sand-bath). On removing the wax the device is etched into the glass.

Extraordinarily small amounts of fluoride can be detected thus, especially if the apparatus is set aside for some hours before warming it.

N.B.—This test will not work in presence of a silicate, with which HF reacts (as it does with glass).

$$4HF + SiO_2 = 2H_2O + SiF_4.$$

In this case the mixture is fused on platinum with excess of fusion mixture, the melt extracted with water, treated with excess of ammonium carbonate (which ppts. the silica after standing for some hours), filtering, exactly neutralising with HCl and evaporating to a small volume. The fluoride is pptd. as CaF_2 by adding $CaCl_2$ and treated as above after filtering and drying.

3. **$AgNO_3$.**—No reaction.

4. **$BaCl_2$.**—White ppt. of BaF_2, except in presence of much ammonium salt.

For solution and analysis of fluorides, see pp. 162, 184.

Fluosilicic Acid, H_2SiF_6.

This acid is formed by the action of silicon fluoride on water.

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + \underset{\text{ortho-silicic acid.}}{H_4SiO_4}.$$

The free acid is decomposed when boiled.

$$H_2SiF_6 = SiF_4 + 2HF.$$

Solubility.—Potassium and barium salts are difficultly soluble in water. The rest are soluble.

Dry Tests.

All fluosilicates are decomposed on ignition.

$$K_2SiF_6 = 2KF + SiF_4.$$

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The SiF_4 is recognised by its reaction with a drop of water, which it covers with a film of silicic acid.

Wet Tests.

1. **Dilute HCl.**—Little or no reaction.
2. **Strong H_2SO_4** decomposes all fluosilicates.

$$K_2SiF_6 + H_2SO_4 = Na_2SO_4 + SiF_4 + 2HF.$$

Test for SiF_4 with a drop of water in the loop of a platinum wire and the HF by the etching test.

3. **$AgNO_3$.**—No reaction.
4. **$BaCl_2$.**—White crystalline ppt. $BaSiF_6$.
5. **KCl,** from not very dilute solutions, ppts. gelatinous K_2SiF_6.
6. **Alkalis** ppt. gelatinous silicic acid from the *free* acid solution; they do *not* neutralise it directly.

$$H_2SiF_6 + 6KOH = 6KF + 3H_2O + H_2SiO_3.$$

7. **NH_4OH** decomposes fluosilicates *themselves.*

$$Na_2SiF_6 + 4NH_4OH = 2NaF + 4NH_4F + H_4SiO_4.$$

There is a further group of acids (sometimes called Group VII.) which are non-volatile, form soluble salts with the alkalis, but have no particular group reagents. These are silicic, tungstic and titanic acids. The two latter are included in the chapter on rare elements.

Silicic Acid, H_2SiO_3 (meta).

Salts corresponding to various hydrates are known amongst the natural silicates.

Solubility.—All silicates except those of sodium and potassium are insoluble in water. Many natural silicates (especially the zeolites) are readily decomposed by dilute acids. Others are only decomposed by fusion with fusion mixture or by treatment with hydrofluoric acid.

Dry Tests.

Silicates fused in a bead of microcosmic salt (on a platinum wire) give an opal bead, the silica being insoluble. (Not infallible, however).

Wet Tests.

I. Silicates of sodium and potassium ("water glass").

1. **Dilute acids** cause a ppt. of metasilicic acid, which, however, is not quantitative, the acid being largely soluble in dilute mineral acids. To separate it completely the solution is evaporated with much HCl, moistened with strong HCl, dried and gently heated.

By this means the acid is partly dehydrated and rendered insoluble in water. (See analysis of Kaolin.)

2. **Ammonium salts** cause a pptn. of silicic acid, as ammonium silicate is immediately hydrolysed by water.

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II. Insoluble silicates.

Those decomposable by dilute HCl are *finely* powdered and boiled with this acid, evaporated dry on the water-bath, treated as in 1 above, and finally extracted with hot water. The insoluble residue is proved to be silica by mixing with CaF_2 and strong H_2SO_4 and warming in a lead test-tube. The SiF_4 evolved renders turbid a drop of water (held on a platinum wire, *not* a glass rod).

Those undecomposable by acids are either

(*a*) Fused with fusion mixture and the melt dissolved in water and treated as in I. 1.

(*b*) Evaporated with a mixture of pure sulphuric and hydrofluoric acids, taking care not to overheat and thus render basic the residual sulphates.

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CHAPTER IV.

RARE ELEMENTS.

ONLY the more common of the rare elements will be considered.

GROUP I.

Thallium, Tl = 204·1.

Source.—Dust from pyrites burners where thalliferous pyrites is used.
Oxides.—Thallous, Tl_2O, basic. Thallic, Tl_2O_3, basic.

DRY TESTS.

Thallium salts moistened with dilute HCl colour the bunsen flame a fine green. The spectrum consists of one green line.

WET TESTS.

I. **Thallous Compounds.**

1. **HCl** ppts. white TlCl, slightly soluble in water. Hence thallium also occurs in Group III. (See No. 3 below.)
2. **NH_4OH or KOH** cause no reaction.
3. **$(NH_4)_2S$** ppts. black Tl_2S quantitatively. Tl_2S is soluble in mineral acids.
4. KI ppts. yellow TlI. Very sensitive test.
5. **K_2CrO_4** ppts. yellow Tl_2CrO_4, insoluble in cold mineral acids (*cf.* lead).

It may also be mentioned that thallous aluminium alum is readily obtained, and that thallium chloroplatinate is yellow and practically insoluble in water. Hence thallium resembles both lead and the alkalis.

II. **Thallic Compounds.**

Obtained practically only by dissolving the oxide in acids. They readily undergo hydrolysis (by boiling the aqueous solutions) into $Tl(OH)_3$ and the acid.

1. **Alkalis** ppt. brown $Tl(OH)_3$.
2. KI ppts. yellow thallous iodide and free iodine.

Tungsten, W = 184.

This metal really belongs to Group II., though the pptn. of its sulphide is difficult and it is therefore pptd. as *sulphide* by $(NH_4)_2S$ followed by acid.

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But as it is usually met with as tungstates, and HCl ppts. insoluble tungstic acid from these, it is found in Group I.

Oxides.—WO_2 (unstable, pyrophoric) brown powder. WO_3 canary yellow. Acid anhydride.

Dry Tests.

A bead of microcosmic salt is colourless in oxidising flame, blue in reducing flame. If reduced further by the introduction of a little $FeSO_4$ it becomes red.

Wet Tests.

Use a solution of sodium tungstate, Na_2WO_4.

1. **Dilute HCl** (and other mineral acids) ppt. white hydrated tungstic acid, H_4WO_5 (*i.e.* WO_3+2H_2O), which turns yellow (H_2WO_4) on boiling. It is insoluble in *dilute* acids. It readily forms a hydrosol (colloidal solution) if washed with water.

N.B.—"Meta" tungstates are often met with. These have the formula, *e.g.* $Na_2W_4O_{13}$, *i.e.* $[Na_2WO_4+3WO_3]$ and HCl does *not* ppt. tungstic acid from this except on prolonged boiling with excess of *dilute* acid.

2. **H_2S.**—No ppt. in acid solutions.

3. **$(NH_4)_2S$.**—No ppt. until solution is *afterwards* acidified, when light brown WS_3 is formed, insoluble in dilute acids.

4. **Reducing agents.**—(*a*) **Nascent hydrogen,** from Zn and dilute HCl causes the formation of a fine blue ppt. which does not change (*cf.* molybdenum).

(*b*) **$SnCl_2$.**—First causes a yellow colour in neutral solutions. On acidifying and warming a fine blue ppt. is obtained (W_2O_5). (*Cf.* Molybdenum.)

RARE ELEMENTS OF GROUP II.

A. The Copper Group.

The "Platinum Metals."

Palladium.

Oxides,—PdO and PdO_2, both basic.

Dry Tests.

All palladium compounds on ignition leave the metal, which can be dissolved in aqua regia and tested as below.

Wet Tests.

I. Palladous Salts.

Use $PdCl_2$.

1. **H_2S** ppts. black PdS, insoluble in $(NH_4)_2S$. Soluble in boiling HCl and in aqua regia.
2. **NaOH (not KOH)** ppts. a brown basic salt soluble in excess.
3. **NH_4OH** ppts. flesh-coloured $PdCl_2(NH_3)_2$, soluble in excess.
4. **KI** ppts. black PdI_2, soluble in excess.

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5. **Reducing agents**, assulphurous and formic acids, alcohol, etc., ppt. the metal.

6. **KCl** ppts. from a strong solution reddish-brown octahedra of K_2PdCl_4.

II. Palladic Salts.

Generally give the same reactions as palladous salts except with:

1. **KCl**, which in strong solutions ppts. yellow needles of K_2PdCl_6.
2. **NH_4Cl** ppts. the corresponding ammonium salt (red).

Osmium, Os = 191.

Oxides.	OsO.	Insoluble in acids.
	Os_2O_3.	" " "
	OsO_2.	" " "
	$[OsO_3]$.	Osmic anhydride, known in its salts only.
	OsO_4.	Perosmic acid anhydride. Soluble in water.

All the oxides, and the metal itself, when heated in air volatilise as OsO_4 (vaporising at 100° C.), which has a characteristic smell like chlorine. This property (shared with ruthenium) of forming volatile oxides distinguishes osmium from the other platinum metals and forms a ready separation.

Dry Tests.

1. See above.
2. Heated in hydrogen, all osmium salts yield the metal which may be recognised as above.

Wet Tests.

Use chlorosmic acid (or the potassium salt) H_2OsCl_6.

1. **H_2S** ppts. dark-brown OsS.
2. **Alkalis** (including NH_4OH) ppt. red-brown hydroxide.
3. **Reducing agents.**—Tannic acid, sulphurous acid and others give a dark-blue colour, due to $OsCl_2$. KI gives a purple colour due to above and free iodine.
4. **Indigo** is decolorised by *perosmic acid.*

B. The Arsenic Group.

Iridium, Platinum, Gold, Molybdenum.

Iridium, Ir = 193.

Oxides.—IrO, Ir_2O_3, IrO_2.

Dry Tests.

Fused with fusion mixture on charcoal, the grey brittle metal, insoluble in aqua regia, is obtained.

Wet Tests.

Use Na_2IrCl_6.

1. **H_2S** decolorises the yellow solution (reduction to $IrCl_3$), with pptn. of sulphur. Then brown Ir_2S_3 is pptd., soluble in ammonium sulphide.

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2. **NaOH** (not KOH) causes a change of colour from red to green; on warming it finally changes to blue.

$$2IrCl_4 + 2NaOH = 2IrCl_3 + NaCl + NaClO + H_2O.$$

3. **KCl** ppts. from strong solutions dark brown K_2IrCl_6. **NH_4Cl** ppts. the dark red ammonium salt.

4. **Reducing agents.**—Some ($FeSO_4$, $H_2C_2O_4$, $SnCl_2$, etc.) produce a green colour ($IrCl_3$).

Others (Zn, formic acid, etc.) reduce it to metal in the absence of mineral acids. (Hence add ammonium acetate first).

Gold, platinum and molybdenum have already been discussed.

RARE ELEMENTS OF GROUP III.

THORIUM, CERIUM, LANTHANUM, DIDYMIUM, YTTRIUM, ERBIUM, BERYLLIUM, TITANIUM, VANADIUM, TANTALUM, URANIUM.

All except beryllium are pptd. as oxalates (from solutions containing not too much dilute mineral acid) by oxalic acid. Hence it is usual to separate these as oxalates by addition of oxalic acid to the filtrate from Group II., thus making Group III. smaller.

Thorium, Th = 232.

Used in incandescent mantles, the ash of which contains about 97% ThO_2. The sources are monazite [Ce, La, Di, Th], PO_4 + some ThO_2, and thorite, $ThSiO_4$ + 50% ThO_2.

These are decomposed with sulphuric acid.

No Dry Tests.

Wet Tests.

Use $Th(SO_4)_2$.

1. **$H_2C_2O_4$** ppts. white $Th(C_2O_4)_2$, insoluble in dilute acids, soluble in boiling ammonium oxalate (large excess).

2. **Alkalis and also $(NH_4)_2S$** ppts. white $Th(OH)_4$, insoluble in the reagent, soluble in dilute acids. ThO_2, the anhydride, is soluble only in *cold* strong H_2SO_4.

3. **K_2SO_4** ppts. a white double sulphate $K_4Th(SO_4)_4,2H_2O$, insoluble in K_2SO_4.

Cerium, Ce = 138·8.

Oxides.—Ce_2O_3 and CeO_2, both basic. Cerous salts white. Ceric salts orange.

Dry Tests.

The borax bead in oxidising flame is coloured dark brown when hot and very light yellow when cold: colourless in the reducing flame.

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Wet Tests.

I. Cerous Salts.

Use cerous nitrate, $Ce(NO_3)_3$.

1. **$H_2C_2O_4$**, as with thorium. Ppt. insoluble in ammonium oxalate.

2. **Alkalis and $(NH_4)_2S$** ppt. white $Ce(OH)_3$ oxidised in the air to yellow $Ce(OH)_4$. $Ce(OH)_3$ is purely basic and soluble in dilute acids. Tartaric and citric acids prevent its pptn. by ammonia or $(NH_4)_2S$, not by KOH.

3. **K_2SO_4** ppts. difficultly soluble white crystalline $3K_2SO_4$, $Ce(SO_4)_3$, insoluble in K_2SO_4.

II. Ceric Salts.

Use ceric ammonium nitrate, $Ce(NO_3)_4$, $2NH_4NO_3$, H_2O.

The orange-red colour of these solutions, and their tendency to form insoluble basic salts, are characteristic.

They are not usually met with in analysis, being specially prepared from cerous salts under certain conditions. If excess of KOH be added to a cerous salt and chlorine be led in, light yellow $Ce(OH)_4$ is formed, which dissolves in *dilute* acids to form ceric salts, but with strong acids behaves as a peroxide, though it dissolves in strong nitric to form ceric nitrate.

Cerous hydroxide ignited in air forms CeO_2, insoluble in acids in this case. As ordinarily met with Ce_2O_3 is cinnamon coloured owing to the presence of praseodymium. (See later).

Cerous salts can also be oxidised in acid solutions by $PbO_2 + HNO_3$, and by persulphuric acid.

H_2O_2 in acid solution reduces ceric salts to cerous, but in alkaline solution oxidises cerous salts. (Add H_2O_2 to a cerous salt, then NH_4OH.) A reddish ppt. resembling $Fe(OH)_3$ is obtained whose composition is doubtful, but probably is a hydrate of CeO_3 (unknown).

Lanthanum, La = 138.

Oxide.—La_2O_3, readily soluble in acids.

Wet Tests.

Use a solution of lanthanum nitrate, $La(NO_3)_3$.

1. **$H_2C_2O_4$**, as with cerium.

2. **NH_4OH and $(NH_4)_2S$** ppt. a white basic compound, difficult to filter.

3. **KOH** ppts. white $La(OH)_3$, unaffected by oxidising agents. (*Cf.* Cerium.)

4. **K_2SO_4** from strong solutions ppts. white crystalline $3K_2SO_4$, $La_2(SO_4)_3$, insoluble in K_2SO_4.

5. **Iodine.**—To a lanthanum salt add acetic acid and ammonia. Wash the slimy basic ppt. with water and treat with solid iodine. A blue colour is obtained (destroyed by acids or alkalis).

DIDYMIUM { Neodymium, Nd = 144. / Praseodymium, Pr = 140.

These two metals are so much alike in properties and so difficult to separate that it will be sufficient to consider the **Didymium** reactions.

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These are the same as those of lanthanum, except that the oxalate is reddish and that the solutions of didymium salts show a characteristic absorption spectrum which should be examined. A solution of didymium nitrate is placed between the source of light and the slit of a spectroscope. If didymium be present in the rare earth oxalates (as it nearly always is) the oxides resulting from the ignition of the oxalates are cinnamon coloured.

Yttrium, Y = 89.

DRY TESTS.

Y_2O_3 is strongly luminous when heated in the blowpipe flame.

WET TESTS.

Use a solution of $Y(NO_3)_3$.

1. **$H_2C_2O_4$** ppts. the white oxalate $Y_2(C_2O_4)_3$, insoluble in excess, slightly soluble in ammonium oxalate, but only with difficulty in dilute HCl.
2. **NH_4OH and $(NH_4)_2S$** ppt. white $Y(OH)_3$, so do **KOH and NaOH.**
3. **K_2SO_4** forms a double salt which is *soluble* in excess of K_2SO_4. Hence separation from Ce, La and Di.
4. No absorption spectrum is given by yttrium.

ERBIUM { Holmium. Thulium. Dysprosium.

DRY TESTS.

Er_2O_3 colours the bunsen flame green, and the flame has a characteristic spectrum, the bright lines of which coincide with the dark lines of the absorption spectrum shown by erbium solutions.

WET TESTS.

Use a solution of Erbium nitrate, $Er(NO_3)_3$.

1. **$H_2C_2O_4$** ppts. light red $Er_2(C_2O_4)_3$.

The reactions with NH_4OH, etc., and K_2SO_4 are similar to those of ythium.

Erbium solutions give a characteristic absorption spectrum, which should be examined.

Beryllium or Glucinum, Be or Gl = 9·1.

Beryllium is *not* pptd. by oxalic acid, and hence is pptd. in its proper place in Group III.

DRY TESTS.

None.

WET TESTS.

1. **NH_4OH and $(NH_4)_2S$** ppt. white $Be(OH)_2$, insoluble in excess.
2. **KOH** gives the same ppt. soluble in excess to form the beryllate, $Be(OK)_2$.

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3. **$(NH_4)_2CO_3$** ppts. a white $BeCO_3$, readily soluble in excess of the reagent (difference and separation from Al, though the separation is not quantitative). The beryllium is repptd. on boiling as a white basic carbonate.

4. **Neither oxalic acid nor ammonium oxalate** ppt. beryllium.

5. **K_2SO_4** gives a double salt, soluble in excess of K_2SO_4.

Titanium, Ti = 48·15.

Oxides.—Ti_2O_2, Ti_2O_3, TiO_2, TiO_3.

The first two are basic, TiO_2 both basic and acidic.

Dry Tests.

Borax bead. Violet in reducing flame, especially if stannous chloride be present; otherwise continued heating is necessary.

Wet Tests.

Use a solution of titanium sulphate.

1. **NH_4OH and $(NH_4)_2S$** ppt. orthotitanic acid, $Ti(OH)_4$, in the cold. It is readily soluble in acids. From hot solutions metatitanic acid, $TiO(OH)_2$, is pptd., almost insoluble in acids.

2. **KOH** reacts similarly, the ppt. being insoluble in excess of potash.

3. **Water.**—All titanium salts are readily hydrolysed. Hence the separation of titanium from iron, etc. Fuse the oxides with $KHSO_4 \rightarrow$ sulphates of the metals. Extract with cold water, filter, dilute largely and boil for an hour. A ppt. of $TiO(OH)_2$ is obtained which forms a colloidal solution if washed with water. Hence wash with acid.

Tartaric and citric acids, etc., prevent the pptn. of titanic acid (see Iron, etc.).

4. **H_2O_2** gives an orange-red colour (or if very small amounts of Ti are present, as in some iron ores and rocks), a yellow colour (*cf.* Vanadium). This is the most characteristic test for Ti.

5. **$K_4Fe(CN)_6$** gives a brown ppt.

6. **Zinc** in acid solutions (HCl) gives a violet colour.

$$2TiCl_4 + 2H = 2HCl + 2TiCl_3.$$

Titanium will be pptd. as metatitanic acid in Group III. according to the method described in Table III. It will be found with NiS and CoS, and will be left as an insoluble ppt. when these are dissolved in aqua regia. It may be treated as described in No. 3 above. If Table III. A is used (preferable if Ti or Va are present), it will be found with the ppt. of Fe, Cr, and Al hydroxides as metatitanic acid, insoluble in dilute cold HCl. Hence separation and detection.

Vanadium, Va = 51·2.

Oxides.—V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5.

First three basic, last two acidic, anhydrides. The acidic anhydrides are the most important. In V_2O_5 the resemblance of vanadium to phosphorus is clearly shown. V_2O_4 (hypovanadic anhydride) is a blue powder, V_2O_5 is an orange-red crystalline fusible substance.

Ortho-, meta- and pyro-vanadates are known, as also are poly-vanadates, in which the element resembles Cr. The latter are similar in colour also to the dichromates.

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Dry Tests.

Borax bead. Yellow in oxidising flame, green in reducing flame. Considerable vanadium is necessary to colour the bead.

Wet Tests.

Use a solution of an alkali meta- or pyro-vanadate.

1. **$(NH_4)_2S$** turns the solution brown (sulpho-salts) and V_2S_5 is pptd. on acidification. The pptn., however, is incomplete.

2. **H_2S** in acid solution reduces vanadic acid to vanadyl salts, which are a fine blue.

3. **H_2O_2** gives a similar reaction to titanium, *but the colour is destroyed by excess of H_2O_2.*

4. **Reducing agents.**—Some (SO_2 and H_2S, alcohol, oxalic and tartaric acids, etc.) cause reduction to vanadyl salts.

$$H_2SO_4 + V_2O_5 + SO_2 = \underset{\text{blue}}{V_2O_2(SO_4)_2} + H_2O.$$

Others (HI, Zn, etc.) reduce it still further to green salts of V_2O_3 (only visible in former case after removal of iodine).

Zn and other metals finally reduce the green solution to violet salts of V_2O_2.

5. **NH_4Cl (solid)** ppts. colourless $(NH_4)VO_3$ (metavanadate).

Tantalum, Ta = 181·5.

Oxides.—Ta_2O_4, indifferent. Ta_2O_5. Acid anhydride.

Solubility.—Ta_2O_5 is very insoluble after ignition, and the only way of getting it into solution is by fusion with KOH (silver crucible).

Dry Tests.

None.

Wet Tests.

Use potassium hexatantalate.

1. **NH_4OH and $(NH_4)_2S$** ppt. from *acid* solutions of tantalates either tantalic acid or acid ammonium tantalate according to the excess of ammonia (prevented by tartaric acid).

2. **Dilute HCl** ppts. tantalic acid from strong solutions, readily soluble in excess of acid. Dilute H_2SO_4 partially ppts. tantalic acid from this solution.

3. **Dilute H_2SO_4** ppts. tantalic acid almost quantitatively on boiling a dilute solution.

4. The best test for tantalic acid is **KF, HF**. To a strong solution of tantalic acid in HF add KF, which ppts. crystalline difficultly soluble potassium fluotantalate K_2TaF_7, which on boiling turns to a white insoluble basic salt.

5. **Nascent hydrogen** (Zn + HCl) does not produce any colour.

Uranium, U = 120.

Oxides.—UO_2 (copper coloured) basic. Forms *uranous* salts when treated with acids *in absence of air, e.g.* $UO_2 + 4HCl = 2H_2O + UCl_4$.

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They are *very readily* oxidised to *uranyl* salts by exposure to air.

$$UCl_4 + O + H_2O = (UO_2)Cl_2 + 2HCl.$$

It will be seen that according to strict definition these are *basic* salts. They are, however, soluble in water, the best known being the nitrate and acetate, which are used in volumetric analysis for the determination of phosphoric acid (*q.v.*).

UO_3 dissolves in acids to form *uranyl* salts and is therefore uranyl oxide. It is acid to strong alkalis, giving their uranates. (See below.)

U_3O_8 (dark green) dissolves in acids out of contact with air, forming a mixture of uranyl and uranous salts. It is therefore $2UO_3 . UO_2$. It occurs as *pitchblende.*

$$2U_3O_8 + 4H_2SO_4 = 2(UO_2)(SO_4)_2 + U(SO_4)_2 + 4H_2O.$$

All uranium salts are yellowish-green, similar to the well-known uranium glass.

Dry Tests.

Yields a yellowish-green borax-bead.

Wet Tests.

Use uranyl nitrate or acetate.

1. **$(NH_4)_2S$** ppts. brown uranyl sulphide $(UO_2)S$, soluble in acids and in ammonium sulphide or carbonate.

2. **NH_4OH** ppts. yellow ammonium uranate.

$$2(UO_2)(NO_3)_2 + 6NH_4OH = 4NH_4NO_3 + 3H_2O + \begin{matrix} UO_2—ONH_4. \\ > O \\ UO_2—ONH_4. \end{matrix}$$

3. **KOH** ppts. yellow potassium uranate similarly.

4. **$K_4Fe(CN)_6$** ppts. brown uranyl potassium ferrocyanide $(UO_2)K_2Fe(CN)_6$.

5. **Na_2HPO_4** ppts. pale yellow uranyl phosphate $(UO_2)HPO_4 \cdot (UO_2NH_4PO_4$ in presence of ammonium acetate).

6. **$BaCO_3$** ppts. all the uranium in the cold. (Composition of the ppt. doubtful: probably basic carbonate).

Uranium is pptd. in Group III. as ammonium uranate and is separated from the other metals of this group as the same compound.

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CHAPTER V.

COURSE OF ANALYSIS.

THE student is strongly advised to follow the procedure set out below.

A. To obtain a thorough knowledge of the reactions of the ions by first analysing substances containing not more than one base and one acid. In this list also the elements themselves may be included, also free acids, free bases and neutral oxides, and simple insoluble compounds (*not* complex insolubles).

B. To obtain a thorough knowledge of the separation of the radicals into their groups by analysing mixtures of several bases and acids of which not more than one occurs in any one group.

C. To proceed to a knowledge of the separation of radicals in the same group by analysing mixtures containing more than one base or acid in the same group.

D. To obtain a knowledge of the necessary deviations from the usual separations which the presence of certain substances, especially phosphoric, oxalic, boric, hydrofluoric and several organic acids renders necessary.

E. To obtain some knowledge of the reactions and separations of the more common rare elements.

The methods to be followed in each of the above cases will now be discussed. The student cannot be too strongly warned against simply getting a mechanical knowledge of the "tables," the chemistry of which he does not understand. This will be guarded against as far as possible by explanations of the principles involved in the separations, etc., before proceeding to the actual experiments.

A. ANALYSIS OF SIMPLE SALTS, ETC.

The actual course of analysis is as follows:

1. Heat the substance in a small tube of hard glass closed at one end, and observe any changes that take place, identifying any gases, etc., evolved.
2. Heat the substance on charcoal as explained previously.
3. Borax bead test, if necessary.
4. Dilute hydrochloric acid test on the dry substance.
5. Strong sulphuric acid test on the dry substance (if necessary).
6. Confirmatory tests for the acid: 1st, $AgNO_3$; 2nd, $BaCl_2$, then any others.

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7. Confirmatory (group) tests for the base. First the group reagents, then confirmatory tests.

After performing the first five of the above tests the student should usually have a fair idea as to what the substance is, and should know what to expect in 6 and 7.

With regard to the carrying out of 6 and 7, the following cases arise:

I. **The substance is soluble in water.**—Test with litmus. If acid, the substance is not necessarily an acid, or even an acid salt. It may be a normal salt of a weak base (all except alkalis and alkali earths).

If alkaline, the substance is either a soluble base or an alkali salt of a weak acid, such as carbonic, boric, hydrosulphuric, phosphoric, sulphurous, etc.

II. **The substance is insoluble in water, but soluble in dilute acids.**—In this case the confirmatory tests for acids of Groups II., III. and IV. cannot be carried out (if it is necessary to do so) on the original substance. The acid must therefore be brought into a water-soluble form (*i.e.* converted to its sodium salt) by boiling the substance with some sodium carbonate solutions, filtering, exactly neutralising the filtrate with *nitric* acid and carrying out the tests with this neutral liquid.

III. **The substance is insoluble except in strong acids or in aqua regia.**—In this case the action of the concentrated acid may destroy the original acid, *e.g.* certain sulphides are soluble only in strong nitric acid or aqua regia, in which case the sulphide is destroyed; or, again, it may alter the character (valency) of the base, *e.g.* Hg_2Cl_2 must be dissolved in aqua regia, when it becomes mercuric chloride. In cases like these the student must learn by experience what alternatives present themselves; a good idea should have been obtained from the preliminary tests.

The *acid* in substances of this class may have to be tested for as in case II., and the base may have to be tested for in the residue which is left on the filter when the substance is boiled with sodium carbonate and filtered. It will be present as carbonate, basic carbonate or oxide, and may therefore be dissolved in dilute nitric acid (after thorough washing) and the base tested for in this solution.

IV. **The substance is insoluble.**—It is fused on a piece of broken porcelain (or on platinum foil, unless a reducible metal be present) with excess of fusion mixture (in a few cases caustic alkali may be necessary). The melt is extracted with hot water, filtered, the acid tested for in the filtrate and the base in the residue, as already indicated in II. and III.

Simple insoluble substances are AgCl (AgBr, AgI), $BaSO_4$, $SrSO_4$, $PbSO_4$, SiO_2; freshly ignited Al_2O_3, Cr_2O_3, SnO_2; some ferro- and ferricyanides, *e.g.* prussian and Turnbull's blue; artificial SnS_2 (mosaic gold). (For details of treatment see page 164.)

Confirmatory Tests for Acid.

The systematic search for acids according to groups will generally be found unnecessary.

The action of dilute HCl and of strong H_2SO_4 on the dry substance will have indicated the acid sufficiently to enable the necessary confirmatory tests to be applied at once.

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The acids which give no visible test with either of the above reagents are:

Sulphuric, phosphoric, boric, arsenious, arsenic, antimonious, antimonic and silicic (in insoluble silicates).

These should be tested for separately in the above order.

It should be remembered that if the base is in Group I. (which will have been shown by the charcoal tests), barium *nitrate* and *nitric* acid must be used as a test for sulphuric acid, otherwise an insoluble ppt. of the chloride of the base is formed, which may be mistaken for $BaSO_4$.

It is much better, however, to add barium chloride to the solution of the substance in dilute HCl. In this case no mistake can be made, for salts of Group I. metals will not (apparently) dissolve in dilute HCl, a ppt. of the chloride forming at once. If this is found to be the case, *then* confirm sulphuric acid by making a fresh solution in dilute HNO_3 and adding $Ba(NO_3)_2$.

It is very necessary to know whether phosphoric, oxalic or hydrofluoric acids are present before proceeding to the Group tests, or misleading results may be obtained in Group III. (See below.)

Should the student desire to work through the group tests for acids the following is the scheme.

A. The original aqueous neutral solution of the acid radical (prepared if necessary by the action of sodium carbonate as already indicated) is treated with $AgNO_3$.

1. *No ppt.* The acid is in Group V. or VI.

2. *A ppt.* First make sure that the ppt. is "genuine" by adding water and warming. If it dissolves it is silver sulphate, nitrite or acetate, caused by the use of too strong a solution and the limited solubility of these salts.

If the ppt. is a "real" one, the next step is to see if it is soluble in dilute HNO_3, best done by taking a *fresh* portion of the original solution and adding *first* HNO_3, *then* $AgNO_3$.

1. *No ppt.* The acid is in Group II. or III. (or VII.).

2. *A ppt.* The acid is in Group I.

B. The original aqueous neutral solution is treated with $BaCl_2$. ($Ba(NO_3)_2$ if the base is in Group I.).

1. *No ppt.* The acid is in Groups I., II. or V. (or VII.).

2. *A ppt.* First make sure that it is "genuine" as in A 2. above (for $BaCl_2$ and $Ba(NO_3)_2$ are pptd. sometimes if a *strong* solution of a chloride or nitrate is used, owing to the limited solubility of these and the Mass Law).

If it is a ppt. find out whether it is soluble in dilute HNO_3 (best by adding dilute HNO_3 to a fresh portion of the original solution and then some $BaCl_2$).

1. *No ppt.* The acid is in Group III. or IV. (or VII.).

2. *A ppt.* The acid is in Group VI.

Apply confirmatory tests.

The possibility of there being *no acid radical present* (substance is an element, base, neutral or peroxide) should not be forgotten. The preliminary tests indicate the presence of these.

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Confirmatory Tests for Base.

A. NOT MORE THAN ONE BASE AND ONE ACID PRESENT.

Dissolve the substance in water, and add dilute HCl to a small portion. If a white ppt. is obtained, the base is in Group I.

If the substance is insoluble in water, the following solvents should be tried:

1. **Dilute HCl,** first cold, then hot. A small pinch of the finely-powdered substance is added to half a test-tube of the solvent; only thus can it be seen whether it is soluble or not. If it dissolves only in hot dilute HCl, cool the solution under the tap. A white crystalline ppt. on cooling will be lead chloride, and the substance may be litharge, etc., lead carbonate, or some basic salt of lead.

2. **Strong HCl,** first cold, then hot. (Procedure as in 1.) Several sulphides, insoluble in dilute HCl, are soluble in strong HCl, though somewhat slowly, *e.g.* HgS, Sb_2S_3, etc. The H_2S evolved will usually be masked by the HCl fumes, and should therefore be tested for with a filter-paper soaked in an alkaline lead solution (add excess of NaOH to lead acetate solution). H_2S causes a dark stain of PbS. Strong HCl is also the correct solvent for several ignited oxides, especially Fe_2O_3, which dissolve slowly in the dilute acid.

3. **Dilute HNO_3.**—This is useful in the case of a few sulphides which are not readily soluble in HCl. It would also be the correct solvent for oxides, carbonates, etc., of bases in Group I., which do not dissolve readily in HCl for obvious reasons (page 25), also for Cu_2O.

4. **Aqua regia.**—To 1 c.c. of strong HNO_3 add 4 c.cs. of strong HCl and warm gently. $3HCl + HNO_3 = 2H_2O + NOCl + Cl_2$.

The "nascent" chlorine is the main factor in the solvent action.

This solvent will be necessary for some sulphides, *e.g.* HgS, etc. Also for mercurous chloride, which is oxidised to mercuric chloride.

The student is again reminded that solvents 3 and 4 may alter the valency of a metal; in the case of mercurous mercury making it appear in Group II. instead of in Group I.

The above solvents should always be tried in the order indicated.

To prepare the solution add about as much of the finely-powdered substance as will cover a sixpence to the minimum amount of solvent necessary to dissolve it. In case water or dilute HNO_3 is the correct solvent, add some dilute HCl to a *portion* of the solution. A white ppt. shows the base to be in Group I.

N.B.—Remember that thiosulphates ppt. *sulphur.*

If no ppt. is obtained with dilute HCl, pass H_2S into *the same portion.* A coloured or black ppt. shows the base to be in Group II.

If strong HCl is the solvent, dilute with thrice its volume of water before passing H_2S.

N.B.—Oxidising agents, such as nitrous or nitric acids, ferric salts, chromates, free halogens, especially chlorine left from aqua regia (which should have been evaporated nearly dry and taken up in water), also sulphurous acid, etc., cause a ppt. of sulphur. This is nearly always *white*, but may sometimes be yellow. An idea as to what to expect should have been obtained from the preliminary tests.

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If no ppt. is obtained with H_2S throw away the portion used, and to a *fresh* portion of the original solution add ammonium chloride and ammonia. Note any ppt. and to it add a drop of ammonium sulphide (or better, pass H_2S for a few moments), and note any change of colour.

The colour, etc., of the ppt. should give some idea of what is present.

N.B.—The salts (except those of the alkalis) of certain acids, especially phosphoric, oxalic, and hydrofluoric, and a few chromates, especially barium, are not soluble in water, but in dilute HCl. On neutralising this HCl by ammonia, the original salt is pptd.

E.g.

$$Ca_3(PO_4)_2 + 6HCl = 3CaCl_2 + 2H_3PO_4.$$

$$3CaCl_2 + 2H_3PO_4 + 6NH_4OH = Ca_3(PO_4)_2 + 6NH_4Cl + 6H_2O.$$

Hence it is necessary to know whether these acids are present or not before coming to Group III. or the beginner may be misled.

If no ppt. is obtained with NH_4OH or $(NH_4)_2S$, to the *same* solution add $(NH_4)_2CO_3$ and boil. A white ppt. shows the presence of Group IV.

If no ppt. is obtained with $(NH_4)_2CO_3$, to the same solution (cooled) add Na_2HPO_4 and rub the sides of the tube with a glass rod. A white crystalline ppt. shows the presence of magnesium.

If no ppt. is obtained with Na_2HPO_4, the *original solution* must be tested for sodium, potassium and ammonium, separately; the two former by the flame test and their reagents; the latter by (*a*) grinding a portion of the solid with quicklime in a mortar, or (*b*) by heating with NaOH solution, both of which cause the evolution of ammonia. NaOH, however, will cause ammonia to be evolved from *amides* as well as ammonium salts.

Having found to which group the base belongs, the next thing is to apply confirmatory tests.

I. *The ppt. is in Group I.*

Allow it to settle, pour off the liquid, wash the ppt. once with cold water, decant, add some more water and boil.

(*a*) *The ppt. dissolves.*—It is $PbCl_2$.

(*b*) *The ppt. does not dissolve.*—It is AgCl or Hg_2Cl_2. Allow to settle, decant and treat with ammonia. If the ppt. dissolves, it is AgCl; if it turns black it is Hg_2Cl_2.

Apply confirmatory tests to the *original solution*, noting especially the action of KOH.

N.B.—The ppt. may possibly be TlCl or WO_3 (the rare metals of Group II.). Apply confirmatory tests to the original solution.

II. *The ppt. is in Group II.*

If black, it is CuS, or HgS.

If yellow it is CdS, As_2S_3 or SnS_2.

If dark brown it is Bi_2S_3 or SnS.

If orange, it is Sb_2S_3.

Decant and wash once as before, and if yellow, orange or dark brown add one or two c.cs. of yellow ammonium sulphide and warm.

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The ppt. dissolves.—The base is in Group II. B.

The ppt. does not dissolve.—The base is in Group II. A. Perform confirmatory tests on the original solution. In case As or Sb are known to be present do not use KOH, which may give misleading results (see p. 94). If not, note especially the action of KOH added dropwise till present in excess.

III. *The ppt. is in Group III.*

A. Phosphoric, oxalic, etc., acids are known to be absent.

I. *The ppt. was formed on addition of NH_4OH.*

(*a*) Did not change on adding H_2S [or $(NH_4)_2S$]. The ppt. is $Al(OH)_3$ or $Cr(OH)_3$.

(*b*) It went black on adding H_2S. The ppt. is $Fe(OH)_2$ or $Fe(OH)_3$ (according to its original colour).

II. *The ppt. was not formed until H_2S was added.*

(*a*) It is black. NiS or CoS.

(*b*) It is white. ZnS.

(*c*) It is buff or flesh coloured. MnS.

N.B.—$Mn(OH)_2$ is soluble in NH_4Cl, but on standing in the air, or in the presence of oxidising agents, a brown or black ppt. of $MnO(OH)_2$ forms.

Apply confirmatory tests (especially KOH as before) to the *original solution.*

B. Phosphoric, etc., acid is present.

In this case the original salt is pptd. on adding NH_4OH. The original acid must be identified. If it is hydrofluoric, it must be got rid of in the manner described under confirmatory tests for this acid.

If the acid is chromic, the ppt. will be $BaCrO_4$. The original solution must be boiled with plenty of dilute HCl and some alcohol, which reduces it to chromic chloride and barium chloride. The chromium is pptd. as $Cr(OH)_3$ by adding NH_4Cl and NH_4OH, boiling well in a basin, and filtering. The $Cr(OH)_3$ is rejected and the filtrate is tested for barium by adding $(NH_4)_2CO_3$. Confirmatory tests (dilute H_2SO_4) are made on the original solution.

If the acid is oxalic, the dry salt should be cautiously heated, when CO is evolved and a carbonate is left, which is dissolved in dilute acid and this solution used for the group tests.

If the acid is phosphoric, the ppt. caused by NH_4OH may be the phosphate of iron (very pale yellow), chromium (green), aluminium, manganese, nickel (green), cobalt (blue), barium, strontium, calcium or magnesium (all white). Zinc phosphate is *soluble* in NH_4Cl. The colour should be noted, and the action of H_2S (or $(NH_4)_2S$) tried. The phosphates of Fe, Ni or Co turn black, due to the formation of sulphide. The phosphate of manganese turns flesh coloured (MnS), and ZnS is *pptd.* (white). $AlPO_4$ (white), $CrPO_4$ (green) and the phosphates of Ba, Sr, Ca and Mg remain unaltered.

We have therefore only to decide between the phosphates of Al, Ba, Sr, Ca and Mg.

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To the original solution add KOH dropwise till in excess. If the white ppt. first formed dissolves in the excess of alkali, the base is Al. If not, it is Ba, Sr, Ca or Mg.

To see which, to the solution of the original substance in *acetic* acid add much $CaSO_4$ solution.

(1) An immediate ppt. (slight one only) = $BaSO_4$.

(2) A gradual (slight) ppt., especially on gently warming and standing for a few minutes = $SrSO_4$.

(3) No ppt. = Ca or Mg.

To see which, to original solution (which will be in dilute HCl) add dilute H_2SO_4 and an equal bulk of alcohol. A white ppt. = $CaSO_4$. No ppt. = Mg.

To confirm any of the above four metals, the original phosphate is boiled with some sodium carbonate solution for several minutes. The liquid is filtered, the residue of the metallic carbonate is *well* washed with hot water, dissolved in dilute acetic acid and the usual confirmatory tests applied.

N.B.—The rare metals are not included in the above.

IV. *The ppt. is in Group IV.*

To the original solution in water (or *acetic* acid if insoluble in water) add much $CaSO_4$ solution.

An immediate ppt. = Ba.
A gradual ppt. = Sr.
No ppt. = Ca.

Apply confirmatory tests to the original solution.

V. *The ppt. is in Group V.*

In this case the ppt. is the confirmatory test, there being no group reagent for Group V., which has been discussed above.

The possibility that there is *no base present* (the substance is a non-metallic element or a free acid) should not be forgotten. The preliminary tests will indicate the absence of these.

Insoluble Substances.

These consist of:

Silver halides and cyanide. AgCl, AgBr, AgI and AgCN (not AgF).

Sulphates of Ba, Sr and Pb.

Oxides of Al and Cr (Al_2O_3 and Cr_2O_3) native or ignited.

Silica, SiO_2, native TiO_2, native or ignited SnO_2 and Sb_2O_4 (partly soluble in hot strong HCl).

Mosaic gold, SnS_2.

Silicon, carbon, carborundum (CSi).

Many silicates.

Prussian and Turnbull's blue (soluble, however, after long treatment with aqua regia) and other complex cyanides.

Sulphur is soluble by long treatment with strong HNO_3, but is not treated thus. It is unmistakable.

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Of the above substances, Cr_2O_3 and SnS_2 are unmistakable in appearance, and the silver halides are readily fusible.

Silver, lead and tin will also be found in the preliminary tests.

The above substances are brought into solution by special methods depending on the substance.

Silver compounds are fused in a crucible and when cold treated with dilute sulphuric acid and a piece of zinc, thereby being reduced to metallic silver. This is dissolved, after washing, in hot dilute HNO_3. The acid (except hydrocyanic) will be found in the filtrate. Hydrocyanic is recognised in the preliminary tests.

Lead sulphate is soluble in boiling KOH solution. H_2S ppts. lead sulphide from the filtrate, and the acid is found in combination with the potassium. It may also be fused with fusion mixture. (See below.)

Barium and strontium sulphates are fused with several times their weight of fusion mixture, either on platinum foil or a clean piece of a broken porcelain basin. The melt is quickly extracted with hot water, filtered and the filtrate acidified with dilute HNO_3 and tested with $BaCl_2$.

The residue of carbonate on the filter is washed thoroughly with boiling water and dissolved in dilute nitric acid. This solution is tested for Ba or Sr in the usual way.

Tin dioxide and tin disulphide.—Are either (1) Heated in hydrogen, and reduced to tin, which is dissolved in moderately strong HCl, or (2) Fused with KCN, and reduced to tin, or (3) Fused with fusion mixture and sulphur, the tin being thereby converted into Na_2SnS_3 (thio-stannate), soluble in water, whence HCl ppts. SnS_2 in acid-soluble form.

Antimony tetroxide is treated as in (3) for tin.

Al_2O_3 and Cr_2O_3.—These are fused with $KHSO_4$.

$$2KHSO_4 = H_2O + K_2SO_4 + SO_3,$$

being thereby converted into sulphates. The melt should dissolve in water. (Chromite, FeO, Cr_2O_3, is treated thus).

Alternatively, they may be fused with fusion mixture, with addition, in case of Cr_2O_3, of some KNO_3. Sodium aluminate, $Al(ONa)_3$, and sodium chromate are thereby formed.

(1) $Al_2O_3 + 6Na_2CO_3 = 2Al(ONa)_3 + 6CO_2$.

(2) $Cr_2O_3 + 2Na_2CO_3 + 3O$ (from KNO_3) $= 2Na_2CrO_4 + 2CO_2$.

The melt is extracted with water, filtered if necessary, and the filtrate

(1) Acidified with HCl and made alkaline with ammonia, which ppts. $Al(OH)_3$.

(2) Acidified with acetic acid and tested for chromate with lead acetate or barium chloride.

TiO_2 is fused with fusion mixture, whereby sodium metatitanate is formed, insoluble in water, but soluble in HCl.

Insoluble silicates are decomposed by fusion with excess of fusion mixture (they must first be *very* finely powdered). The melt is treated with water and the whole (soluble and insoluble suspension) acidified strongly with HCl

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and evaporated dry. It is then moistened with strong HCl and again dried. It is then treated with hot dilute HCl and filtered.

Residue is SiO_2 (partly hydrated).

Solution contains the chlorides of the bases.

Insoluble complex cyanides are decomposed by boiling with KOH in a basin. The hydroxide of the base will be left, the acid going into solution. Dilute, filter and confirm.

Calcium fluoride, etc., may be decomposed by evaporating with strong H_2SO_4 and treating the residual sulphate as may be necessary ($CaSO_4$ dissolved in dilute HCl, $BaSO_4$ as above, etc.).

Carbon.—Burn in oxygen and bubble product through lime-water. *Graphite* will not burn in air, and not easily in oxygen. It may be mixed with KNO_3 and heated in a hard glass tube and the gases evolved bubbled through lime-water.

Silicon dissolves in molten fusion mixture.

$$Si + Na_2CO_3 + \underset{\text{(from air)}}{O} = \underset{\text{(soluble in water)}}{Na_2SiO_3} + CO.$$

Carborundum, CSi.—Fuse the finely-powdered substance with alkali in a silver crucible.

$$CSi + 4KOH + \underset{\text{(from air)}}{O_2} = K_2CO_3 + K_2SiO_3 + 2H_2.$$

Test for carbonate and silicate in the product.

B. ANALYSIS OF MIXTURES CONTAINING NOT MORE THAN ONE BASE OR ACID IN THE SAME GROUP.

In this case the bases must be separated and the confirmatory tests applied to each after separation. It may or may not be necessary to separate the acids; they can generally be tested for separately. A few of the more important separations will be discussed.

The preliminary tests are carried out as before, except that heating in a closed tube may not give any characteristic results.

If the substances can be separated by the use of different solvents, this should be done, and the solution of each is analysed as above for simple substances.

If not, it is necessary to separate them by means of the **group reagents.** The ppts. are washed and dissolved in suitable solvents and confirmed in the usual way.

The separation of the bases into their groups is carried out as follows :—

(*N.B.*—This table is used *however many* bases may be present in *any* group.)

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TABLE A.—SEPARATION OF THE BASES INTO GROUPS. (Phosphoric Acid absent.)

The solution of the bases is treated with dilute HCl till no more ppt. forms, filtered, and ppt. washed with dilute HCl.

Ppt.—May be

$AgCl$, Hg_2Cl_2, $PbCl_2$, $TlCl$, H_2SiO_3, H_2WO_4 — white.

Sb_2S_3, Sb_2S_5 — orange.

SnS_2 — yellow.

The three last would be pptd. by HCl from a solution of the sulpho salts in water, *e.g.* K_3SbS_4, etc.

See under each metal for solvents and confirmatory tests.

See also p. 171.

Filtrate.—Must be freed from halogens, sulphur dioxide, nitrous and much nitric acid, which oxidise H_2S with pptn. of sulphur. This is accomplished by evaporating nearly dry and taking up in water and dilute HCl. Too much HCl must not be present, or the pptn. of PbS, Sb_2S_3 and SnS_2 will be incomplete. About 5 c.cs. of 4N . HCl per 100 c.cs. of solution is about right. If chromic acid be present, it must be reduced to a chromic salt by boiling with HCl and alcohol (CrO_3 oxidises H_2S). Then see if Group II. be present by passing H_2S into a test portion, warming and again passing H_2S. (This is to avoid missing arsenic acid, *q.v.*) Ferric salts cause a ppt. of sulphur, being reduced to ferrous salts. If Group II. is absent, reject the test portion, and proceed to Group III. with the main portion. If Group II. be present, transfer the whole solution to a small conical flask, fitted with a two-holed rubber stopper carrying two tubes, one reaching nearly to the bottom of the flask, the other just long enough to pass through the stopper. Attach the long tube to the H_2S kipp, allow the air to be swept out by a stream of the gas, and close the short tube with the thumb. Shake vigorously for a minute, allow more H_2S to pass in, and repeat the shaking. In this way the pptn. takes place with a minimum waste of H_2S and time. Filter and wash the ppt. with very dilute HCl containing H_2S.

Ppt.—May be

HgS, CuS, PbS — black.

Bi_2S_3 — dk. brown.

CdS — yellow.

(Insoluble in alkali polysulphide.)

As_2S_3 or $_5$ — yellow.

Sb_2S_3 or $_5$ — orange.

SnS — dk. brown.

SnS_2 — yellow.

AuS — black.

PtS — black.

Mo_2S_3 — brown.

(Soluble in alkali polysulphide.)

See p. 172-5.

Filtrate.—Should smell of H_2S, or pptn. may be incomplete. Boil off the H_2S in a basin (test steam with lead acetete paper), add NH_4Cl and NH_4OH till alkaline. **Avoid a *large* excess of NH_4OH. Note colour of ppt.** (if any) and pass H_2S as above. Note **any further ppt. or change of colour. Just raise** to boiling (in the flask), filter and wash **ppt. with NH_4Cl or NH_4NO_3 solution.**

Ppt.—May be

$Al(OH)_3$ — white.

$Cr(OH)_3$ — greenish grey. or under some conditions violet.

FeS — black.

MnS — flesh coloured.

ZnS — white.

NiS, CoS — black.

UO_2S — brown.

$Ti(OH)_4$ — white.

See p. 176-7.

Filtrate.—It is better (though not absolutely necessary) to free the solution from ammonium sulphide by evaporating somewhat after rendering acid with HCl. Then filter from deposited sulphur, **and add NH_4OH till alkaline, and** then $(NH_4)_2CO_3$ till no more ppt. falls. **Boil and filter. Wash ppt. with hot water.**

Ppt.—May be

$BaCO_3$, $SrCO_3$, $CaCO_3$ — White.

See p. 178-9.

Filtrate.—May contain one of the bases Mg, Na, K, Li. Divide into two parts:

1. To smaller part add Na_2HPO_4, and rub sides of tube with a glass rod. White crystalline ppt., which *may* be some minutes appearing, is $MgNH_4PO_5 . 6H_2O$.

2. Larger part. Evaporate dry and ignite gently on a gauze to drive off ammonium salts. (Mg salts form insoluble basic salts.) If a residue is left, flame-test it. **Yellow flame = Na, Lilac = K, Crimson = Li. Dissolve the main portion of the residue in a *little* water, filter through a very small filter, and apply confirmatory tests, especially for potassium.**

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TABLE B.—PHOSPHORIC ACID PRESENT.

In this case the ppt. in Group III. would contain mixed phosphates. It is therefore necessary to get rid of the phosphoric acid before pptg. Group III. The filtrate from Group II. is therefore freed from H_2S, and any iron present is oxidised to the ferric state by boiling and adding a few drops of strong HNO_3. Add NH_4Cl, transfer to a flask, and add NH_4OH dropwise till a permanent ppt. just forms. Now add enough dilute HCl to dissolve this ppt., and then several c.cs. of a saturated solution of ammonium acetate. The HCl is thus replaced by acetic acid, in which the phosphates of Fe^{III}, Cr and Al are insoluble. Boil (otherwise $AlPO_4$ may not be properly pptd.), cool and filter.

Ppt.—May be

$FePO_4$ (pale yellow).
$CrPO_4$ (green)
(pptn. will usually not be complete),

or

$AlPO_4$ (white).

To confirm, dissolve in HCl, add *slowly* excess of NaOH, and boil.

A red ppt., $Fe(OH)_3$.

A green-grey ppt. forming from a green solution on boiling, $Cr(OH)_3$.

A white ppt., soluble in excess of NaOH, not pptd. on boiling, $Al(OH)_3$.

Filtrate.—$FeCl_3$ solution is added *dropwise*, the solution being placed in a white basin. At first $FePO_4$ is pptd. When all the phosphoric acid is thus thrown down, the next drop of $FeCl_3$ gives a red colour of ferric acetate, causing the liquid to turn salmon-pink. (*Avoid excess of $FeCl_3$.*) Dilute and boil for several minutes, adding water to keep up the original volume. The ferric acetate is hydrolysed to a basic insoluble salt. Filter. The filtrate, which should be free from iron, is now ready for analysis, starting at Group III.

An alternative method of getting rid of phosphoric acid is as follows:

Evaporate Group II. filtrate dry, add 10-15 c.cs. of strong HNO_3 and then 1-2 gms. of tin. Boil to a small volume. Test a drop with molybdate to see that the phosphoric acid is pptd. If not, repeat with addition of more acid and a little more tin. Now dilute considerably and filter. The phosphoric acid forms an insoluble compound of doubtful composition with the meta-stannic acid.

The filtrate must now be freed from Pb and several other Group II. metals (introduced as impurities in the tin) by treatment with H_2S and filtering. The filtrate, freed from H_2S, is ready for analysis at the beginning of Group III.

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TREATMENT OF THE GROUP PPT.

(*See under each metal for solvent for group ppt. and confirmatory tests.*)

Ppt. is in Group I.—Pour boiling water into the filter. If the ppt. dissolves it is $PbCl_2$. Confirm by testing this solution.

If it does not dissolve, pour a little warm ammonia solution into the filter.

(*a*) The ppt. dissolves; it is AgCl. Repptd. by HNO_3.

(*b*) The ppt. turns black; it is Hg_2Cl_2. Confirm by usual tests (copper-foil test best here). Treat blackened ppt. with HCl and boil with a piece of copper-foil.

For rare metals, see under each metal. The ppt. of silicic acid will mean that the filtrate must be freed from this, as described on p. 164.

Ppt. is in Group II.—If yellow, orange or dark brown, warm a portion with yellow $(NH_4)_2S_2$. If it dissolves it is As_2S_3 or $_5$, Sb_2S_3 or $_5$, SnS, SnS_2.

If yellow and insoluble, it is CdS.

If black, it is CuS, PbS, HgS.

The correct solvent for CdS, CuS and PbS is the minimum of hot dilute HNO_3. Apply confirmatory tests to this solution.

The correct solvent for HgS is a *little* aqua regia. Evaporate the solution nearly dry, dilute with water and apply confirmatory tests to this.

If the ppt. is CdS, confirm by the "flash" tests.

If the ppt. is As_2S_3 or Sb_2S_3, confirm by "flash" tests, etc. (See under each metal.)

As. may be confirmed by dissolving the ppt. in a little warm NH_4OH and H_2O_2, whereby it is oxidised to ammonium arsenate. Evaporate just dry, take up in water and confirm by adding silver nitrate.

(The H_2O_2 should be free from HCl, or the silver arsenate may be masked by white AgCl.)

Tin is confirmed by dissolving in the least amount of warm, strong HCl (freeing from H_2S), and to a portion adding KOH dropwise till in excess. A ppt. forms, soluble in excess of alkali.

To see whether stannous or stannic, to the other portion add 1 or 2 drops of $HgCl_2$. White ppt. of Hg_2Cl_2 shows it to be stannous; no reaction, stannic.

A black ppt. in Group II., soluble in ammonium sulphide, may be gold or platinum sulphides. Solvent, aqua regia.

Note that the other rare metals of Group II. (platinum metals excepted) are *not pptd.* by H_2S in acid solution, except molybdenum, the pptn. of which takes a long time. No difficulty will therefore be experienced with these metals in this group. The correct way to ppt. them is to add $(NH_4)_2S$ till the ppt. is redissolved, and then acidify with HCl. (This is done *after* the separation by H_2S from acid solution.) It will, of course, bring down NiS and CoS if present. These are, however, readily confirmed by the preliminary tests.

N.B.—Sometimes when the group ppt. is tested with ammonium sulphide, it *apparently* turns black. This is due to the presence of iron, nickel or cobalt in the mixture, and to insufficient washing of the Group II. ppt. from the solution of these metals.

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SEPARATION OF THE ACIDS IF NOT MORE THAN ONE OF ANY ONE GROUP IS PRESENT.

TABLE C.—SILVER NITRATE SEPARATION.

The original neutral aqueous solution (prepared if necessary by boiling the substance with Na_2CO_3, etc., is tested with $AgNO_3$. If no ppt., Groups I., III. and IV., but not necessarily II., are absent. If a ppt. forms, Groups I., II., III. and IV. may be present. Recall solubilities of silver sulphate, nitrite and acetate (esp. two latter). Treat a portion with hot water.

It dissolves.	**It does not dissolve.** Groups I., III. and IV. may be present.
Groups I., III. and IV. are absent. Group II. possibly present.	Treat the remainder with warm dilute HNO_3 (poured into the filter, allowed to run through and poured over again).
	Ppt. is wholly soluble. Group I. is absent. | **Ppt. is partly or wholly insoluble.** Group I. is present. Filter.

To the solution if wholly soluble, or to the filtrate if partly soluble in dilute HNO_3, add carefully a dilute mixture of ammonia and alcohol, so that it floats on the acid liquid. (The alcohol is to assist this.) Somewhere at the junction a neutral zone will be formed. If a ppt. is seen here, Groups III. and IV. may be present. The colour of the ppt. will indicate to some extent what acid is present, and should confirm previous deductions from preliminary tests. Confirmatory tests should then be carried out.

N.B.—Boric acid will not be pptd. in presence of ammonium salts, and will be missed here. It must be tested for separately. (See under that acid.)

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Ppt. is in Group III.—The colour of the ppt. or the *change* of colour on passing H_2S is fairly conclusive, except that Ni and Co both give black ppts. with H_2S, and none with NH_4Cl and NH_4OH.

The solvents for the ppts. in this group are:

Dilute HCl for all except NiS and CoS. Boil off the H_2S produced before applying confirmatory tests.

Aqua regia for NiS and CoS. Boil just dry and redissolve in water before applying confirmatory tests.

Ppt. is in Group IV.—Dissolve it in hot dilute acetic acid. See whether it is barium, strontium or calcium by testing with $CaSO_4$. Then apply other confirmatory tests.

The detection of Group V. metals has been indicated in Table A.

TABLE D.—BARIUM CHLORIDE SEPARATION.

The neutral aqueous solution containing the acid radicals is treated with excess of $BaCl_2$aq.

No ppt.	**A ppt. is formed.**—Add dilute HCl and warm.	
Groups III., IV. and VI. absent.	**The ppt. does not dissolve.**—Group VI. is present. Filter.	**The ppt. partly or wholly dissolves.** Note that thio-sulphates and sulphites are destroyed, the former with pptn. of S. Filter if necessary.
	In either case, add to the filtrate KOHaq till exactly neutral.	
	A ppt. forms. Groups III. and IV. are present.	**No ppt. forms.** III. and IV. absent.

The above two tables are not really necessary. The preliminary tests should give indications of *all acids* which may be present except a few non-volatile ones. Those indicated, and those few that are not thus indicated, are readily tested for separately. The possibility of mixtures of acids masking one another should not be lost sight of. (See p. 142.)

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C. ANALYSIS OF MIXTURES CONTAINING MORE THAN ONE BASE IN A GROUP.

The separation of the bases into their groups is carried out as in Tables A or B, according to the absence or presence of phosphoric acid.

Each group ppt. is then treated according to the following methods :

Group I. metals are separated by taking advantage of :

The solubility of $PbCl_2$ in boiling water.
The solubility of AgCl in ammonia.

TABLE I.—Separation of Group I. metals.

The ppt. is treated with boiling water, which is poured into the filter, caught in a boiling tube, boiled up again and poured over it again. Finally wash with boiling water, rejecting washings.

<table>
<tr><td rowspan="2">Filtrate.
Cf. Pb by K_2CrO_4, KI, H_2SO_4, etc.</td><td colspan="2">Residue.—Treat several times (as above) with warm ammonia. If the residue turns black, Hg_2Cl_2 is present.</td></tr>
<tr><td>Filtrate.
Acidify with dilute HNO_3. White ppt. = Ag.</td><td>Residue.—Will be black. Transfer some to a test-tube with a strip of copper-foil and boil. A grey deposit of Hg appears on the foil, which on rubbing takes a bright polish.</td></tr>
</table>

Group II. metals are separated into two portions by the solubility of the thio-acids (sulphides of arsenic, antimony, tin, gold, platinum) in $(NH_4)_2S_2$.

Of those insoluble in this reagent, HgS is insoluble in hot HNO_3.

$PbSO_4$ is insoluble. $Bi(OH)_3$ is insoluble in ammonia.

Cu is "suppressed" by KCN, as H_2S has no action on the cuprocyanides, and CdS is pptd. by H_2S under these conditions.

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TABLE II. (A).—Separation of Group II. Metals.

A hole is made in the filter, the ppt. is washed through into a basin with warm yellow $(NH_4)_2S_2$, and the whole just boiled and filtered.

<table>
<tr><td colspan="3">Residue.—HgS, PbS, CuS, Bi_2S_3, CdS. Wash with H_2S water, make a hole in filter, wash through into a basin with a stream of hot water from wash-bottle, using as little water as possible. Raise to boil, and add hot, strong HNO_3, one drop at a time, with a short wait between each drop. As soon as ppt. has either dissolved (except for a little sulphur) or turned white, filter and wash with hot water.</td><td rowspan="5">Filtrate.
Thio-salts of As, Sb, Sn, Au, Pt.
See Table II. (B).</td></tr>
<tr><td rowspan="4">Residue.
$Hg_2S(NO_3)_2$
Dissolve in a very small quantity of aqua regia, evaporate nearly dry, dissolve in water and confirm.</td><td colspan="2">Filtrate.—The other bases as nitrates. If the solution in HNO_3 is carried out as above, no $PbSO_4$ will be formed. Add dilute H_2SO_4 and evaporate till excess of HNO_3 has been driven off. Dilute with water. If white ppt. present, it is $PbSO_4$. Filter. Wash with very dilute H_2SO_4.</td></tr>
<tr><td rowspan="3">Residue.
$PbSO_4$.
Dissolve in ammoniacal ammonium tartrate and test with H_2S.</td><td colspan="2">Filtrate.—The remaining bases as sulphates. Add excess of NH_4OH. Blue colour = Cu. Ppt. = Bi. Filter; wash.</td></tr>
<tr><td>Ppt.—Basic bismuth sulphate.
Confirm by
(a) Flash.
(b) Von Kobell's reaction.
(c) Dissolving in 1 c.c. of dilute HCl and pouring into a large beaker of cold water. White cloud of BiOCl forms.</td><td>Filtrate.
Add KCN till blue colour disappears. Pass H_2S. Yellow ppt. = CdS. Confirm by flash test.</td></tr>
</table>

Note on Table II. (A).

Copper here is not separated, but suppressed, *after* it has been recognised. It may be pptd. as follows:

To the filtrate from the $Bi(SO_4)(OH)$ add dilute H_2SO_4 till acid. Then add freshly-prepared $Na_2S_2O_3$aq till colourless. (Do this in a small flask standing on a white tile.) Boil for 5 minutes. Cu_2S is pptd. Filter.

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Residue, Cu_2S.	**Filtrate.**
The reactions involved are : (1) The oxidation of the thio-sulphate to tetrathionate by $CuSO_4$, *exactly* as it is by iodine, the $CuSO_4$ being reduced to a cuprous salt, and (2) Immediately dissolved in excess of $Na_2S_2O_3$ to form $Na_4[Cu_2(S_2O_3)_3]$. (3) This, on boiling, is decomposed like the corresponding Ag salt. $Na_4[Cu_2(S_2O_3)_3] = Na_2SO_4 + SO_2 + Cu_2S + S + Na_2S_2O_3$.	Must be freed from SO_2 by boiling. Cool. Pass H_2S. Yellow ppt. $= CdS$. Confirm by flash test.

Separation of Arsenic, Antimony and Tin.

The arsenic sulphide is separated by taking advantage of

(*a*) Its solubility in ammonium carbonate or

(*b*) Its insolubility in hot, strong HCl.

The separation of antimony and tin is effected

(*a*) Electrochemically.

(*b*) By the action of milk of lime on the sulphides.

(*c*) By the solubility of stannic sulphide in oxalic acid.

TABLE II. (B).—Separation of As, Sb and Sn.

The solution of the thio-salts is carefully acidified with dilute HCl (draught-cupboard) and filtered.

$$2(NH_4)_3AsS_4 + 6HCl = 3H_2S + 6NH_4Cl + \underbrace{As_2S_3 + 2S}_{As_2S_5}, \text{ etc.}$$

If this ppt. is black or dark brown, the presence of gold and platinum is indicated.

Filtrate. Reject.	**Ppt.**—Wash with H_2S aq, and transfer to a test-tube with about 25 c.cs. of water and a piece of solid $(NH_4)_2CO_3$, about 5 gms. Warm to 35° C. (in water-bath), and gently agitate till the carbonate has dissolved. It is very necessary that the temperature should not be sufficiently high to decompose the ammonium carbonate into free ammonia and CO_2, as the former will act on the antimony sulphide. Filter and wash.	
	Filtrate Acidify with HCl and pass H_2S. Ppt. $= As_2S_3$. Confirm by solution in ammonia and H_2O_2 or by flash test, etc.	**Residue.**—The sulphides of antimony and tin are transferred to a basin in the usual way, allowed to settle, and the water poured off. They are then dissolved in a little hot, strong HCl, and a piece of pure zinc and a piece of platinum-foil added. The antimony is deposited on the Pt as a black velvety stain, and the tin as a spongy mass on the zinc so *long as contact with the platinum* is kept. Dissolve the antimony in warm nitric and tartaric acids, and cf. by H_2S. Dissolve the tin in HCl and cf. by a *drop or two* of $HgCl_2$.

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Alternative methods for treating the antimony and tin sulphides are as follows:

Oxalic acid Method.

The sulphides (as having been separated) are dissolved in the minimum of hot, strong HCl, boiled well, and the solution made just alkaline with ammonia. Two or three gms. of oxalic acid crystals are added, the solution again boiled and treated with H_2S. Sb_2S_3 is pptd. Filter, cf. Sb in usual way, and neutralise the filtrate with ammonium hydrate, render acid with acetic (or very slightly with HCl) and pass H_2S for the tin. This is Clarke's method.

N.B.—It is essential for this method that the tin should be in the stannic state. If necessary, it should be oxidised to this state by rendering alkaline with potash, adding tartaric acid and H_2O_2 and boiling. Then acidify with oxalic, boil to destroy H_2O_2, and pass H_2S.

Milk of Lime Method.

The mixed sulphides of Sb and Sn (after the separation of As) are washed into a test-tube, allowed to settle, the water poured off, and milk of lime added (about 10 c.cs.). This is gently warmed to 80° for several minutes and filtered.

The antimony dissolves as calcium antimonite and thio-antimonite, the SnS_2 is changed to $Sn(OH)_4$. Filter. Acidify filtrate with acetic acid and pass H_2S for the antimony.

Wash the residue twice with water, once with acetic acid to remove excess of lime, and dissolve the $Sn(OH)_4$ in hot dilute HCl. Add NH_4Cl and NH_4OH. White ppt. of $Sn(OH)_4$, *or* the solution of stannic chloride may be reduced by nascent hydrogen (Zn) and treated with a drop of $HgCl_2$.

N.B.—For this method also the tin *must* be present as SnS_2, as SnS is unacted upon by milk of lime.

Notes on Group II. separation.

1. It is often advised to treat the ppt. with KOH instead of $(NH_4)_2S_2$.

$$M_2S_3 + 6KOH = \underset{\text{(hydrated)}}{M_2O_3} + 3K_2S + 3H_2O \text{ (partly)}$$

The oxides and sulphides then dissolve in the KOH and the K_2S to give mixtures of K_3MO_3 and K_2MS_3. On acidifying the sulphides are repptd.

The objection to $(NH_4)_2S_2$ is that it dissolves small amounts of copper sulphide.

2. If the ppt. formed on acidifying the solution in yellow ammonium sulphide is black (or dark coloured), gold and platinum may be present.

The separation of these from As, Sb and Sn is as follows:

Dry the sulphides, mix with six times their weight of a mixture of 5 parts of NH_4Cl and 1 part NH_4NO_3, place in a porcelain boat and heat in a current of air in the apparatus shown in Fig. 32. (Alternatively, simply heat the dried sulphides in a current of HCl gas in the same apparatus.)

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The chlorides of As, Sb and Sn volatilise and are caught in the flask. The gold and platinum left in the boat are dissolved in aqua regia, just dried, moistened with strong HCl and some chlorine water, dried again on a water-

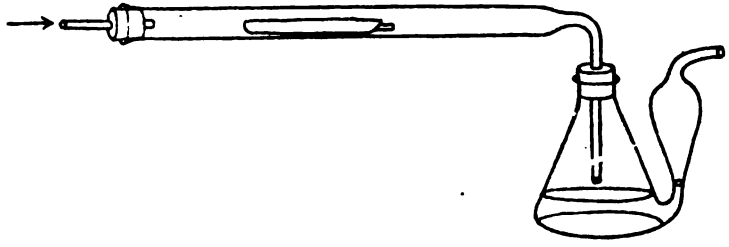

FIG. 32.

bath, and taken up in a little water. We now have solutions of H_2PtCl_6 and $HAuCl_4$. The latter is reduced to gold by warming with

(*a*) Freshly made $FeSO_4$ aq. or
(*b*) Oxalic acid solution, or
(*c*) Treating with cold $H_2O_2 + NaOH$.

The platinum is pptd. from the concentrated filtrate as $(NH_4)_2PtCl_6$ by the addition of NH_4Cl and alcohol.

DETECTION OF SEVERAL ACID RADICALS.

It is very seldom necessary to carry out a systematic *separation*, according to a set scheme, of acid radicals, even when present in the same group.

The following mixtures, however, present some difficulty, and are specially dealt with.

(i) *Chloride, bromide, iodide.*—(See p. 122.)

(ii) *Nitrate in presence of acids which obscure the ring test.*—Use some other test for nitric acid, *q.v.*

(iii) *Nitrate and nitrite.*—The nitrite, having been detected in one portion by the usual reactions, is destroyed in a *fresh* portion by treatment with hydrazine hydrosulphate (the only reagent which does not form traces of nitric acid). The solution is then tested for nitrate.

(iv) *Perchlorate, chlorate and chloride.*

(*a*) Test for chloride.

(*b*) Test for chlorate by the strong HCl test.

(*c*) Boil some of the solution with SO_2 aq. to reduce the chlorate to chloride. Ppt. the chloride with Ag_2SO_4, and neutralise with Na_2CO_3 to remove H_2SO_4 and excess of silver. Filter, evaporate, ignite, dissolve in water and again test for chloride.

(v) *Sulphate, sulphite, sulphide, thio-sulphate.*—Fenton recommends the following:

Shake the neutral solution with excess of $CdCO_3$ and filter (p. 181).

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TABLE III.—SEPARATION OF THE METALS IN GROUP III.

The ppt. may contain FeS, $Cr(OH)_3$, $Al(OH)_3$, NiS, CoS, MnS, ZnS, $(UO_2)S$. Treat with *cold* dilute (dinormal) HCl. Filter.

Residue. NiS and CoS. Wash. Dissolve in minimum of aqua regia. Just dry. Take up in water. Add KCN *dropwise* till ppt. formed *just* redissolves. Boil in basin for two minutes. Then add KOH and Br (in KBr solution). Boil. Filter.

Ppt.	**Solution.**
$Ni(OH)_3$ (black). Dissolve in HCl and cf.	Evaporate dry and cf. cobalt by borax bead.

Filtrate.—Chlorides and $(UO_2)Cl_2$. Boil till free from H_2S. *Pour into* some warm NaOH (not KOH), to which some H_2O_2 has been added. (Do this in porcelain basin.) The liquid should still be strongly alkaline. Dilute with an equal volume of water, and filter.

Ppt. $Fe(OH)_3$. $MnO(OH)_2$. $Na_2U_2O_7$. Dissolve in dilute HCl. Boil off chlorine. Add NH_4Cl, boil in a basin, and add *slight* excess of hot NH_4OH. Filter as quickly as possible to prevent oxidation of manganese.

Ppt. $Fe(OH)_3$. $(NH_4)_2U_2O_7$. Dissolve in HCl and add $(NH_4)_2CO_3$ in excess. Warm gently and filter.

Ppt.	**Filtrate.**
$Fe(OH)_3$. Dissolve in HCl, and cf. by $K_4Fe(CN)_6$.	$[UO_2(CO_3)_3](NH_4)_4$. Acidify with HCl and cf. U by $K_4Fe(CN)_6$.

Filtrate. $MnCl_2$. Divide into two parts and add

(1) Bromine water: $MnO(OH)_2$ pptd.

(2) H_2S. MnS pptd.

Filtrate. $Al(ONa)_3$, $Zn(ONa)_2$, Na_2CrO_4. Add NH_4Cl (solid) and boil. Filter.

Ppt.	**Filtrate.**—If *yellow* render acid with acetic acid, boil and ppt. the chromate by *boiling* $BaCl_2$ (added dropwise). Filter.
$Al(OH)_3$. Cf. by Thenard's Blue reaction.	

Ppt.	**Filtrate.**
$BaCrO_4$. Cf. by borax bead.	Cool and pass H_2S. ZnS (white) is pptd. Cf. by Rinmann's Green reaction.

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TABLE III. A.

Some authorities divide Group III. into two parts, A and B. A consists of the ppt. obtained with NH_4Cl and NH_4OH, B consists of the ppt. obtained on saturating the *filtrate* from A with H_2S. The objections to this method are: (1) the appreciable solubility of $Cr(OH)_3$ in excess of NH_4OH, (2) the slight oxidation of Mn salts in ammoniacal solution to $MnO(OH)_2$, and consequent *partial* pptn. The method, if adopted, is carried out thus:—The filtrate from Group II., after removal of H_2S and oxidation to ferric iron is treated in a basin with NH_4Cl, boiled well, and hot NH_4OH added in the least possible excess. Filter whilst boiling, as quickly as possible.

Ppt.—Hydroxides of Fe^{III}, Cr, Al; and $[NH_4]_2U_2O_7$.
Dissolve in little HCl, and add to excess of boiling NaOH in a porcelain basin. Dilute with water, boil and filter hot.

Ppt. $Fe(OH)_3$, $Cr(OH)_3$, $Na_2U_2O_7$.
Dissolve in minimum of strong HCl and add excess of $(NH_4)_2CO_3$. Just raise to boil and filter.

Ppt. $Fe(OH)_3$, $Cr(OH)_3$.
Test a portion for iron by solution in HCl and adding $K_4Fe(CN)_6$.
Test rest for Cr by fusing on Pt foil with fusion mixture and KNO_3. Dissolve in water, filter, acidify filtrate with acetic acid and test for chromate.
N.B.—A green mass after the fusion indicates Mn.

Filtrate. $(NH_4)_4UO_2(CO_3)_3$
Acidify with HCl and *cf.* U by adding $K_4Fe(CN)_6$.

Filtrate. $Al(ONa)_3$.
Acidify with HCl, ppt. the $Al(OH)_3$ by NH_4OH and *cf.* by Thenard's Blue reaction.

Filtrate.—Add some more NH_4OH and saturate cold with H_2S. *Just* raise to boil and filter hot.

Ppt.—Sulphides of Ni, Co, Mn and Zn.
Treat with cold dilute (dinormal) HCl. Filter.

Residue. NiS, CoS.
Dissolve in minimum of aqua regia and proceed as in Table III.

Filtrate. $MnCl_2$, $ZnCl_2$.
Boil off H_2S and add to excess of warm NaOH. Dilute and filter.

Ppt. $Mn(OH)_2$
Dissolve in HCl and *cf.* by
(1) NH_4OH and bromine water.
(2) NH_4OH and $(NH_4)_2S$.

Filtrate. $Zn(ONa)_2$
Acidify with acetic acid and *cf.* Zn by H_2S.

Filtrate. Proceed to Group IV.

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TABLE IV.

Quantitative separations of Ba, Sr and Ca are long and tedious. They depend upon the solubilities of various salts in alcohol. (See Table IV. (A).) The author finds the following method work well.

The ppt. of the carbonates of Ba, Sr and Ca is dissolved in the minimum of hnt dilute acetic acid. A portion is tested with excess of $CaSO_4$ solution and gently warmed. An immediate slight ppt. shows Ba; a gradual one shows Sr. If Ba is absent, proceed as with the filtrate below. If both Ba and Sr are absent, simply confirm calcium by adding $(NH_4)_2C_2O_4$. If Ba is present, boil the main portion of the solution and add boiling K_2CrO_4 dropwise, until a permanent *orange* tint is obtained. Filter and wash.

Ppt. $BaCrO_4$. *Cf.* (1) by moistening with HCl and flame testing. (2) By dissolving in HCl and adding H_2SO_4.	**Filtrate.**—Cool and add an equal volume of 4N . HCl, followed by $(NH_4)_2SO_4$ aq. Warm gently, stand aside for 10 minutes, filter and wash.	
	Ppt. $SrSO_4$. *Cf.* by boiling with Na_2CO_3 aq, filtering, washing well and flame-testing the residue after moistening with HCl.	**Filtrate.**—Render alkaline with ammonia, acid with *acetic* acid and add $(NH_4)_2C_2O_4$ solution. White ppt. $= CaC_2O_4$.

Note on Group IV.—The addition of HCl before pptg. $SrSO_4$ is to prevent the pptn. of $CaSO_4$ by the $(NH_4)_2SO_4$. As, owever, the acid hinders somewhat the pptn. of $SrSO_4$, not less than 10 minutes must be allowed for pptn. to be complete.

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TABLE IV. A.

An alternative separation is as follows:

Having shown the presence of Ba (and perhaps Sr and Ca) as before, the carbonates are dissolved in HCl and carefully evaporated to dryness (*not ignited*). The mixed chlorides are extracted with absolute alcohol, filtered and washed with absolute alcohol.

Filtrate. $BaCl_2$ *Cf.* by any of the tests for Ba.	**Residue.** $SrCl_2$ and $CaCl_2$. If Sr is found to be present ($CaSO_4$ test on a portion dissolved in water) the chlorides are converted to nitrates by evaporating to dryness with conc. HNO_3 (care not to heat the nitrates strongly !), and extracted with absolute alcohol. Filter. Wash with absolute alcohol.	
	Filtrate. $Ca(NO_3)_2$. Evaporate off the alcohol, dissolve in water and *cf.* by any test for Ca.	**Residue.** $Sr(NO_3)_2$. *Cf.* by any test for Sr.

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TABLE V.

The filtrate from Group IV. ppt. is tested for Mg by adding Na_2HPO_4 to a portion. A *crystalline* ppt. of

$$MgNH_4PO_4, 6H_2O = Mg.$$

(If Mg is present in small quantity, the pptn. may take some time; rubbing the sides of the tube with a glass-rod will assist.)

The main portion of the filtrate is now evaporated dry and all ammonium salts expelled by *gentle* ignition. (During this process $MgCl_2$ forms a basic salt insoluble in water.) Be sure that NH_4 salts do not sublime on the cool portions of the dish, as this frequently results in the tests for K being wrongly interpreted. (See under each metal.) The residue is allowed to cool, dissolved in water and filtered. The residue of MgO and of traces of carbon (from organic bases present in ammonia) is rejected. The filtrate is divided into three portions, which are separately tested for Na, K and Li as follows:

(*N.B.*—Test the *original mixture* for ammonium.)

I. Sodium.	II. Potassium.	III. Lithium.
1. $K_2H_2Sb_2O_7$ gives a white crystalline ppt. from *not too dilute* solutions. 2. Flame test (should be *persistent*).	1. H_2PtCl_6 gives a yellow crystalline ppt. from not too dilute solutions. 2. Sodium picrate. Ditto. 3. Sodium bitartrate gives a white crystalline ppt. from not too dilute solutions. 4. Flame test. *Note.*—1, 2 and 3 are best performed in watch-glasses. Vigorous stirring with a glass-rod assists the formation of the ppt. *Ammonium salts* give very similar ppts.	1. Flame test (spectroscope; moisten with HCl first). 2. Na_2HPO_4 ppts. white Li_3PO_4, *on boiling*, in the presence of a trace of NaOH. Filter, make a bead of the ppt. on Pt wire, add $CaSO_4$ and CaF_2, and heat in hottest part of flame. Red flame = Li.

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Residue. Dissolve excess of $CdCO_3$ with acetic acid. Bright yellow residue of CdS = sulphide.	**Filtrate.**—Add excess of $BaCl_2$ and filter.		
	Ppt.—$BaSO_4$ and $BaSO_3$. Wash and treat with dilute HCl. Filter.		**Filtrate.** — Treat with HCl. Yellow ppt. of S and smell of SO_2 = thio-sulphate.
	Residue. $BaSO_4$.	**Filtrate.** Add bromine water. White ppt. of $BaSO_4$. = sulphite.	

(vi) *Tartrate and citrate.*—Separate the tartrate by adding potassium acetate and acetic acid to the neutral solution, followed by alcohol. Set aside for some time, filter, test ppt. for tartrate and filtrate for citrate in the usual way.

TREATMENT OF ALLOYS.

The correct solvent for an alloy is usually nitric acid (aqua regia for the noble metals and aluminium bronze). In a few cases, however, hydrochloric acid is used; especially with aluminium alloys as duralumin or magnalium: the action of nitric acid on aluminium is feeble. Further, a few metals are rendered "passive" by treatment with nitric acid, notably ferrochrome. It is frequently difficult to attack this even with aqua regia owing to its "passivity."

Alloys of tin and antimony (solder, type-metal, etc.) form metastannic and antimonic acids. The former is quite, the latter almost, insoluble in dilute nitric acid. Hence if a white insoluble residue is obtained when the alloy is treated with nitric acid, the liquid is diluted and filtered. The filtrate is analysed for the remaining metals, the residue is washed and dissolved in dilute hydrochloric acid, and examined for tin and antimony by one of the separations given. Antimony, if present, will also be found in the filtrate, owing to the slight solubility of antimonic acid.

CARBIDES, NITRIDES, ETC.

Carbides treated with dilute HCl or sometimes even with water, evolve hydrocarbon; *e.g.* $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$.

Nitrides treated with water evolve ammonia; *e.g.*

$$Mg_3N_2 + 3H_2O = 3Mg(OH)_2 + 2NH_3.$$

Phosphides treated with water or dilute acids evolve PH_3, recognised by its smell and spontaneous inflammability; *e.g.*

$$Ca_3P_2 + 3H_2O = 3Ca(OH)_2 + 2PH_3.$$

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Silicides evolve SiH_4 similarly (spontaneously inflammable).

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

Note.—The correct solvent for ferro-silicon (cast iron, etc.) is aqua regia, if the loss of silicon is to be avoided.

Arsenides may evolve arsine.

$$Zn_3As_2 + 6HCl = 3ZnCl_2 + 2AsH_3.$$

(Nitric acid would, however, naturally be used for these.)

Borides.—Some metallic ones may give hydrogen boride. Many borides require an oxidising fusion to attack them at all.

D. MODIFICATIONS NECESSITATED BY THE PRESENCE OF CERTAIN ACIDS.

1. The case when *phosphoric acid* is present has been discussed. (See Table B.)

2. If *oxalic acid* is present, it is easily missed in the strong sulphuric acid test, as frequently other gases may be evolved which will prevent the carbon monoxide burning.

An oxalate may be confirmed by boiling the substance with sodium carbonate solution, acidifying the filtrate with *acetic* acid, boiling and adding boiling calcium chloride. A white ppt. $= CaC_2O_4$. This is decomposed by hot dilute sulphuric acid (after filtering and washing) and potassium permanganate added dropwise. The reagent is decolorised in the usual characteristic way.

Oxalic acid is removed before making the solution for analysis by *gently* igniting the substance. All oxalates give off carbon monoxide and leave carbonates or oxides.

Remember that ignition may form insoluble aluminium and chromium oxides if salts of these metals are present.

If the oxalic acid is not removed it will be pptd. in Group III. if any metals except the alkalis are present.

3. A further difficulty arises when non-volatile organic matter is present (including many common acids, as tartaric and citric). The pptn. of some metals in Groups II. and III. is thereby hindered or entirely prevented (*e.g.* copper, iron, chromium, aluminium).

These are also destroyed by ignition before making the solution. The carbonaceous residue should be burnt off. This leaves a residue of metallic oxides (metals in some cases). There should be no difficulty in distinguishing metals; in any case dissolve in a little hot strong hydrochloric acid, filter if necessary, and analyse the filtrate as usual. Any insoluble residue will be Al_2O_3, Cr_2O_3, SiO_2, or metals insoluble in HCl, as lead and silver. Al_2O_3 and Cr_2O_3 are fused with $KHSO_4$ as already described under insoluble substances; SiO_2 is examined by itself; lead, silver, etc., are dissolved in nitric acid.

Note that volatile metals will be lost by this process. These will have

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TABLE VI.—THE RARE EARTHS.

Though these have already been placed in groups (see before), it is usual to separate them as oxalates before pptg. Group III. The process is as follows :

The filtrate from Group II., after removal of H_2S and *excess* of HCl (by boiling), is boiled and treated with oxalic acid, added dropwise, till no more ppt. forms. Filter and wash.

<table>
<tr><td rowspan="3">Filtrate.
Remaining groups.</td><td colspan="3">Ppt. Oxalates of Ce, La, Di, Y and Er. Wash, dry and ignite. A mixture of the oxides is obtained. (A cinnamon colour indicates Di.) Dissolve in as little conc. HNO_3 as possible, reduce ceric salt to cerous by adding alcohol, evaporate to a syrup on water-bath, take up in water and allow to stand overnight with solid finely-powdered K_2SO_4. Filter and wash with saturated K_2SO_4 aq.</td></tr>
<tr><td colspan="2">Ppt. Ce, La and $Di_2(SO_4)_3$, $3K_2SO_4$. Dissolve in a little very dilute HCl, ppt. as oxalates by $H_2C_2O_4$, wash, dry and ignite to oxides. Dissolve in a little HCl, ppt. with NaOH, avoiding excess, and lead in Cl_2. Filter and wash.</td><td rowspan="2">Filtrate. Y and $Er_2(SO_4)_3$,$3K_2SO_4$. Ppt. as oxalates, wash, dry and ignite to oxides. Dissolve in HNO_3. Examine absorption spectrum. Er shows characteristic spectrum.
(Place test-tube containing the dissolved nitrates in front of spectroscope slit, between it and the source of light.)
Note.—Erbium being present, Yltrium will also be present.</td></tr>
<tr><td>Ppt. $Ce(OH)_4$.
Wash, dissolve in HNO_3, decolorise with H_2O_2, and add NH_4OH.
A brown ppt. $=CeO_3$, H_2O.</td><td>Filtrate. Acidify with HCl. Ppt. oxalates. Ppt. = La and Di.
Dissolve in HNO_3.
Di shows characteristic absorption spectrum if solution of nitrate is examined. (See under Erbium.)</td></tr>
</table>

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been discovered, if present, in the preliminary tests, and should be confirmed separately.

The possibility of insoluble bodies being present *before* the ignition should be borne in mind. These may be separated by dissolving the rest in the necessary solvent. The filtrate, containing the organic acids, etc., is evaporated dry, the residue ignited and treated as above described.

4. *Hydrofluoric acid is present.*—As calcium fluoride is soluble in hot dilute hydrochloric acid, it will be pptd. in Group III. and will ultimately be found (in part) with the NiS and CoS. Any residue left when these are dissolved in *aqua regia* may be tested for fluoride in the usual way, and the sulphate left may be tested for calcium.

Some will also have dissolved along with the iron, manganese, etc. After boiling off H_2S, add dilute sulphuric acid. A ppt. = $BaSO_4$ or $SrSO_4$. Filter. To filtrate (or to whole if no ppt.) add an equal bulk of alcohol. A ppt. = $CaSO_4$. Filter and treat in the usual manner.

N.B.—It is necessary to carry out the above only when hydrofluoric acid is known to be present. It should have been found in the preliminary tests.

5. *Thio-acids are present.*—In this case HCl will ppt. As_2S_3, Sb_2S_3 or SnS_2 in Group I. These ppts. will readily be recognised and may be treated as in Table II. (B).

6. *Acids of Group VII. are present.*—The necessary treatment for silicic and tungstic acid has been described under these acids, *q.v.*

E. THE SEPARATION OF THE RARER ELEMENTS.

Most of these have already been discussed under their own headings or in the base separation table. The rare earth separation is given here. It should be borne in mind that this separation is incomplete.

Literature.

Systematic Introduction to Qualitative Analysis. WALDEN AND LAMBERT. (Thornton, Oxford.)
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Foundations of Analytical Chemistry. OSTWALD. (Macmillan.)
Notes on Qualitative Analysis. FENTON. (C. U. Press.)

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BOOK III.

QUANTITATIVE ANALYSIS (INORGANIC).

PART I.

GRAVIMETRIC METHODS.

CHAPTER I.

INTRODUCTION AND MANIPULATION.

GRAVIMETRIC analysis consists in obtaining the substance to be estimated in a form of exactly known composition, which is weighed and the amount of substance present calculated. Thus hydrochloric acid or chlorides can be converted to silver chloride, which contains 35·46 parts of chlorine in 143·34 parts of silver chloride.

If a weight w grams of the chloride be taken, and p grams of silver chloride are finally obtained, the weight of chlorine in this is obviously $\frac{35{\cdot}46p}{143{\cdot}34}$ gms. The percentage of chlorine in the original substance is therefore $\frac{35{\cdot}46p \times 100}{143{\cdot}34 \times w}$. Further, it is a simple matter to calculate the amount of original chloride present (instead of chlorine), as will be obvious to the student.

The whole art of gravimetric methods lies in obtaining the *whole* of the required substance in a suitable form of *known composition* and of a *high degree of purity*. These forms are usually ppts., but in a few cases soluble solids are obtained. Precipitates are most easily handled, and the reaction is always carried out in *dilute solution* (of the order of 1-2 %), to prevent the adsorption of soluble bodies by the ppt. Moreover, an excess of the reagent is usually employed for reasons already discussed. (See Solubility product, p. 76.)

Some ppts. are dried at 100°-120° and weighed on a tared filter. Others are strongly heated, the filter being completely burnt and the weight of its ash deducted from the final weighing.

Other methods avoid the use of filter paper altogether.

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The necessity for absolute cleanliness and care in weighing and manipulation is urged upon the student. The following points are so obvious that they should not need more than the mere mention.

1. *Distilled water* is *always* understood when *water* is mentioned.

2. A good balance and an *accurate* set of weights are necessary. *Never* touch weights with the fingers.

It is not absolutely essential that the weights should be accurately to standard so long as they are relatively accurate, *i.e.* the 10 gm. weight must be exactly double the 5 gm. weight, and so on. Methods for testing this are fully described in various papers. (See Richards, *Jour. Am. Chem. Soc.*, 1900, xxii. p. 144, also the section on Physical Chemistry of this book.)

3. A good quality of filter must be used. Suitable filters are sold for the purpose, and the weight of the ash should not exceed 1 milligram.

4. It is never necessary for any of the experiments herein described to weigh more accurately than to the nearest 0·1 milligram. In all calculations *accurate* (not approximate) atomic weights must be used.

5. When a separation is being performed, it is necessary, on filtering and washing the ppts., to add *all* the washings to the filtrate, no matter how bulky the latter may become. It can be evaporated.

6. The student is supposed to understand how to weigh accurately.

7. Hard glass beakers, etc., should be used. Silica glass is desirable in all cases where the reagents, etc., do not attack it.

MANIPULATION.

1. **Weighing.**—The substance to be analysed is weighed out from a weighing bottle. The best form is that shown in Fig. 33. The stopper is ground to fit *outside* the bottle, so that fragments of substance do not adhere to the rough surface of the ground glass. The whole is made of thin "test-tube" glass. The bottle containing the

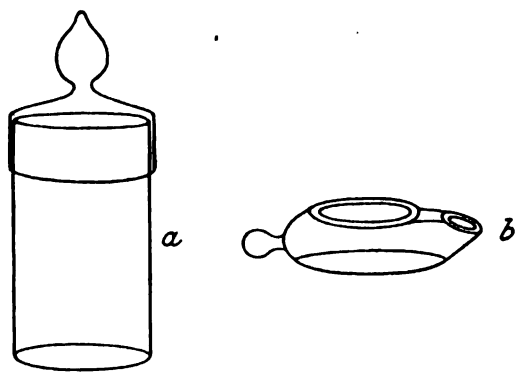

FIG. 33.

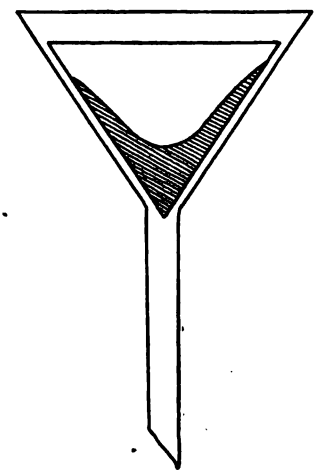

FIG. 34.

substance is weighed, the required amount tipped out into the vessel in which the work is to be done, and the bottle again weighed. *The greatest*

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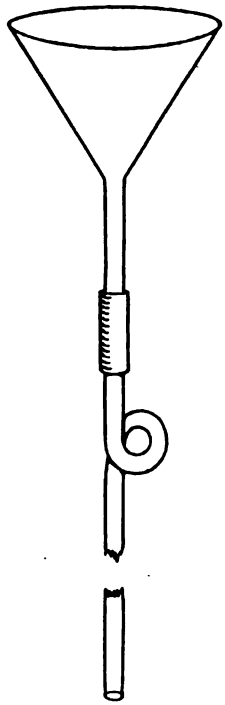
care must be taken that the whole of the substance removed from the bottle is employed in the analysis.

2. **Filtration.**—The size of filter used should be adjusted to the size of the ppt., *not* to the volume of filtrate. The ppt. should occupy a portion of the filter shown approximately in Fig. 34, and should not reach to the top. At least 5 mm. should be quite clear. The filter should not reach to the top of the funnel. It should be very carefully fitted to the funnel, and wetted with hot water before use.

Artificial aids to filtration (filter pump, etc.) are not recommended, but a gentle suction may be used, provided that the ppt. is not of a gelatinous nature. It is necessary to support the filter on a platinum cone, which may be made by cutting a circle of platinum foil of about 4 cms. diameter, as shown in Fig. 35, and folding it into a cone. This is fitted into the funnel and the paper fitted above it. Gentle suction may be obtained by attaching to the funnel a tube 50 cms. long, bent as shown in Fig. 35.



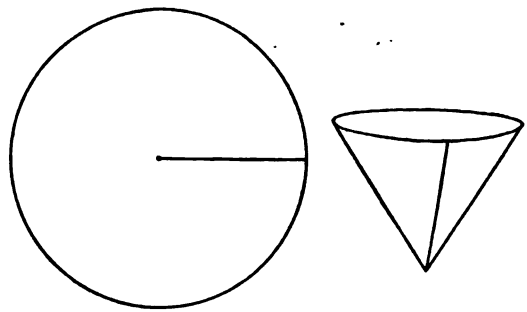


FIG. 35.

The ppt. is washed by means of the wash-bottle, shown in Fig. 36 *a*. The delivery tube should be of such a length that when the neck of the flask is grasped with the thumb, third and fourth fingers and the palm, the jet can easily be grasped between the first and second fingers and guided as desired. It is an advantage to wrap the neck of the flask with thick string, so that boiling water may easily be employed.

The minimum of wash-water necessary for complete removal of mother-liquor is used by allowing the filter to drain completely before adding more. A simple calculation will show that this is more effective than adding fresh wash-water before the previous lot has run through the filter. It is usual also to wash the ppt. by decantation once or twice before finally transferring to the filter. Needless to say, all liquids and washings are decanted *through the filter*. Four washings on the filter may be regarded as the *minimum*. After this, a few c.cs. of the washings may be caught in a test-tube from time

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to time and tested for the substance in solution. When this can no longer be detected by a *sensitive* reaction, the washing may be considered complete.

The *slightest possible* smear of vaseline under the lip of the beaker (outside) will prevent drops of liquid from running down the outside.

Always pour the liquid into the filter *down the stirring rod*, which should be held so that the liquid enters the filter without splashing. Both funnel and beaker, and if necessary the vessel in which the filtrate is being received, should be covered with a clock-glass to exclude dust.

Allow the funnel stem to touch the side of the vessel holding the filtrate, in order to avoid drops splashing up and out of the vessel.

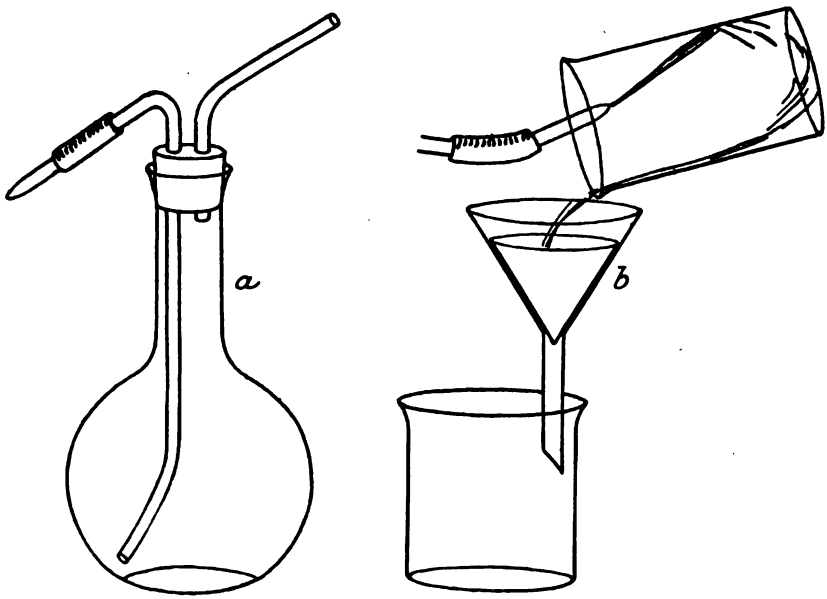

FIG. 36.

Minute portions of a ppt. will almost always cling to the sides of the vessel so that the force of the jet from the wash-bottle will not remove it. A rubber "policeman" is fixed to the stirring rod for the removal of this ppt.

The last portions are washed into the filter as shown in Fig. 36 *b*.

Drying and burning the filter and ppt.—If the ppt. will stand a high temperature without decomposition, the filter is treated as follows. When washing is complete, a filter on which the particulars of the ppt. are written in pencil is wetted with water, placed over the top of the funnel, folded down and the whole placed in a water or steam oven till dry.

Meanwhile a clean porcelain, platinum or quartz crucible (according to the nature of the ppt.) and lid are heated to the temperature to which the ppt. is finally to be heated, allowed to cool somewhat, and placed, by means of the crucible tongs, in a desiccator, to cool completely. It is then transferred to the balance case, allowed to remain there 10 minutes, and weighed.

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A piece of glazed paper (black for white ppts., yellow for black ones) is placed on the bench, and the crucible is placed on the paper. The filter is taken from the funnel, and as much of the ppt. as possible transferred to the crucible. The ppt. is loosened from the filter by rubbing together the inside

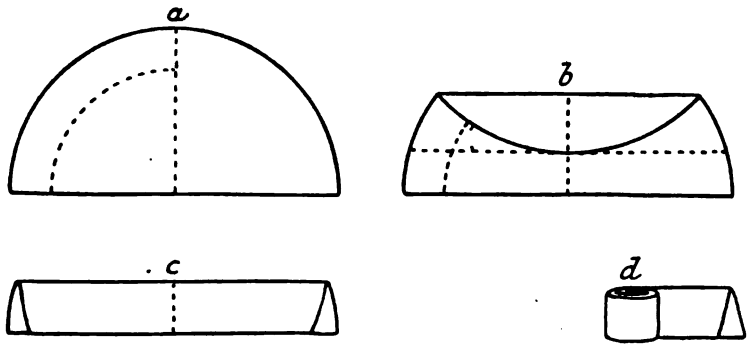

FIG. 37.

surfaces of the cone by means of the thumbs and first fingers of both hands. The crucible is then covered with a funnel to exclude dust. The filter is folded as shown in Fig. 37 (ppt. inside) and finally rolled into a neat tight roll, care being taken not to crack it. A platinum wire is wrapped round the roll, it is held over the crucible and touched with the bunsen flame. Allow the filter to burn as completely as possible without further heating, and burn the carbonaceous residue completely to a white ash by touching it occasionally with the flame. A gentle shake causes the ash to fall into the crucible, any fragments adhering to the wire are removed by a feather or small camel-hair brush, and any fragments that have fallen on to the paper (to be avoided) are swept into the crucible by the same means. The crucible and contents are then ignited at the necessary temperature *till the weight is constant.* Cooling always takes place in a desiccator.

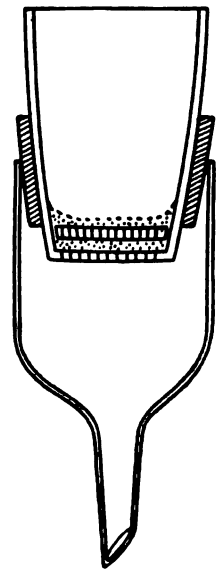

FIG. 38.

Ppts. which will not stand a high temperature may be dried up to 110° on a tared filter. The filter is tared as follows. It is carefully folded, placed in a weighing bottle, and heated to the temperature necessary in the final treatment. Cool in desiccator and weigh. Then fit into the funnel. The filter and ppt. are dried in the funnel at 100°, transferred to the weighing bottle and dried at the required temperature to constant weight.

The Gooch crucible avoids the use of filter-paper. It is not desirable to use it when ppts. have to be ignited. The crucible is shown in Fig. 38. Soft asbestos fibres, purchased for the purpose, are boiled with strong hydrochloric acid, drained and washed thoroughly in a funnel on a filter plate, and dried.

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A portion is shaken with water in a flask so that a thin cream is formed. The Gooch crucible is fitted into its adapter, and attached to the filter flask and pump. *Gentle suction only* is to be used.

Pour some of the asbestos cream into the crucible; drain off the water. Place the small filter plate on the layer of asbestos so formed, and deposit another layer on the plate. Neither layer should exceed 2 mm. in thickness. Wash thoroughly with water and dry at the temperature required finally and weigh. The filtration and washing are performed in a similar manner, *gentle* suction only being used. After washing, dry at the necessary temperatures to constant weight.

Ppts. which are not reduced by the combustion of the filter may be ignited wet, by simply transferring the wet filter and ppt. to a *platinum* crucible, putting the lid on, and drying by heating the crucible some distance above the flame. The crucible is then lowered gradually into the flame, and the tem-

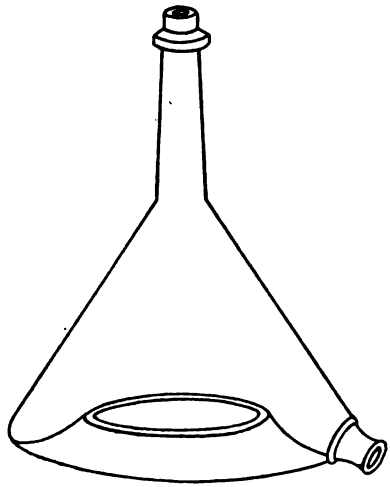

FIG. 39.

perature increased till all volatile matter has come off. Finally the lid is arranged so as to deflect the flame into the inclined crucible, and the ignition completed, the flame being moved slowly so that every part of the crucible is heated and the filter completely burnt. The filter ash must be pure white.

As regards the quantity of substance to be taken for analysis, it should be regulated by the weight of the ppt. As a rough guide, half a gram of final dry ppt. is a maximum convenient amount, but in the case of bulky ppts. less should be obtained.

It is rarely that the pptn. will take place from a solution of more than 2 % strength. Regulate the size of the beaker accordingly. It should never be much more than half full.

Heating and evaporating.—Beakers should not be heated over the naked flame. Even when a gauze is used it is courting disaster to heat *small* quantities of liquids in large beakers. For such purposes an iron plate ($\frac{3}{8}$ inch) about a foot square, supported on a four-legged iron stand and heated in the

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centre with a burner, is useful. The plate should be covered with asbestos paper, or beakers are easily cracked when placed on it.

A beaker containing not too small a quantity of liquid may be heated on a gauze and a *small* flame. Violent ebullition is to be avoided. During all boiling or effervescence the vessel should be covered with a clock-glass, which is afterwards rinsed into the vessel by a jet from the wash-bottle.

Evaporations should be carried out on the water-bath, as ebullition is obviously to be avoided. A funnel such as that shown in Fig. 39, is inverted over the vessel to prevent dust getting into the liquid.

Occasionally evaporations have to be carried out in crucibles. These are rather troublesome as it is difficult to avoid bumping and "creeping." The former may be avoided where possible by using a water-bath fitted with a cone to take a crucible. The latter is overcome by a steam coil of brass tubing into which the crucible fits, the upper portion thus being kept at a temperature which will at once evaporate any liquid which may creep up the sides.

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CHAPTER II.

SOME TYPICAL ESTIMATIONS.

THE student is advised to carry out the following typical examples before attempting a systematic course. In all cases where an estimation is being performed for the first time, it should be carried out on a pure substance of exactly known composition so that the result can be checked.

Similarly, when studying separations they should first be performed on mixtures of known composition, and the results carefully checked. Errors of more than 0·1 % should be usually regarded as due to faulty manipulation.

It is perfectly easy to obtain results well within this limit of error.

N.B.—It will be noticed that many of the separations described in this book are quite different from those used in qualitative analysis. The reasons are two :

(i) *Separations which are sufficiently quantitative in qualitative work are* not *always accurate enough for exact work, though all the separations described in Book II. are fairly so.*

(ii) *The ppts. obtained by using the tables of Book II. are* not always of sufficiently definite composition *for use in quantitative work.*

Determination of Iron (Form : Fe_2O_3). *Use ferrous ammonium sulphate.*—Weigh out about 1·5 gms. of the salt into a 400 c.cs. beaker. Dissolve in 100 c.cs. of water with the addition of 10 c.cs. of 4N sulphuric acid. Cover with a clock-glass and raise nearly to a boil. Oxidise to the ferric state by the addition of nitric acid, one or two drops at a time, till the dark colour disappears and the solution is a clear deep yellow. Care should be taken that loss is not caused by the effervescence that takes place when the nitric acid is added. It should be poured down the stirring rod, the clock-glass cover being displaced as little as possible.

Now rinse the cover into the beaker with a jet of hot water from the wash-bottle. Add 25 c.cs. of 4N ammonium chloride, and then a slight excess of ammonia. Boil for a minute and allow ppt. to settle. Decant the liquid through a filter, wash ppt. once by decantation with hot water (decanting through the filter), and finally transfer to the filter by the help of wash-bottle and "policeman," as already explained on p. 188. Wash with boiling water till a few c.cs. of the washings no longer react with barium chloride. Dry at 100°. Transfer ppt. to a weighed porcelain crucible that has been heated strongly in the bunsen flame before weighing. Burn the filter, add the ash to the crucible, and ignite with bunsen flame to constant weight. The result is Fe_2O_3.

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N.B.—Do not heat with blow-pipe, as there is danger of converting some of the product into Fe_3O_4.

Calculate the percentage of iron in the salt employed.

$$Fe : Fe_2O_3 = 55{\cdot}84 : 159{\cdot}68.$$

Percentage of iron in ferrous ammonium sulphate = 14·24.

Determination of aluminium (Form : Al_2O_3). *Use pure potash or ammonia alum.*—Use 2-2·5 gms. of the salt. Remember that $Al(OH)_3$ exists in a hydrosol form. To prevent this carry out the pptn. in the presence of ammonium nitrate (better than chloride), and wash with dilute ammonium nitrate solution containing a little ammonia. Otherwise the procedure is similar to that in the case of iron. The ppt. should be ignited wet as described on p. 190, in a platinum crucible that has been heated with the blowpipe before weighing. The final ignition is carried out with the blowpipe to constant weight. The ignition may if desired be performed exactly as with the iron ppt. The product is in any case weighed as Al_2O_3.

Determination of chromium (Form : Cr_2O_3). *Use chrome alum.*—Employ about 1·75 gms. Remember that $Cr(OH)_3$ is appreciably soluble in excess of ammonia. Employ the least possible excess, and boil for several minutes until the steam only just smells of ammonia.

Ignite ppt. wet, finishing over the blowpipe to constant weight, and weigh as Cr_2O_3.

Chromates and dichromates must first be reduced to chromic salts. This is done by adding dilute sulphuric acid and passing in sulphur dioxide, or by boiling with hydrochloric acid and alcohol.

The following methods avoid reduction.

Determination of chromic acid (Forms : Cr_2O_3 : $BaCrO_4$). *Use pure potassium dichromate.*

(1) The acid is pptd. as mercurous chromate, and ignited to Cr_2O_3.

Dissolve about ·5-·75 gm. of the salt in 100 c.cs. of water. Treat with a slight excess of pure mercurous nitrate solution. Raise to a boil (see p. 85). Allow ppt. to settle, cool, filter, wash with water containing a little mercurous nitrate, dry at 100°. Separate the ppt. as completely as possible from the filter before burning the latter. Ignite gently at first, finally with blowpipe. Owing to mercury vapours coming off, the first ignition should be carried out in the draught-cupboard. The final residue is pure Cr_2O_3.

$$Cr_2O_3 : 2CrO_3 = 152 : 200.$$

Calculate the percentage of CrO_3 in the salt.

N.B.—This method should not be used in the presence of anything else that gives a ppt. with mercurous salts.

(2) The acid is pptd. as $BaCrO_4$ by adding barium chloride to the solution acid with acetic acid.

The solution of the dichromate is rendered alkaline with ammonia and then just acidified with acetic acid. It is boiled and treated with boiling barium chloride added dropwise, till just in excess. Allow to cool and filter through a Gooch crucible, with *very gentle suction*. Wash with 10 % alcohol, dry at 100°, and finally heat gently to bare redness by placing the Gooch crucible in

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a larger crucible by means of an asbestos ring (see Fig. 43) and heating the outer crucible to full redness.

N.B.—This method cannot be used in the presence of a sulphate.

Determination of copper (Forms : CuO, Cu_2S, $Cu_2(CNS)_2$). *Use pure copper sulphate.*

(1) **As CuO.**—Weigh about 1·5 gms. of the salt into a 400 c.c. beaker. Dissolve in 120 c.cs. of water to which a few drops of dilute sulphuric acid have been added. Raise almost to a boil, and add dropwise, with constant stirring, 2N caustic soda solution (also hot), till no further ppt. forms. Avoid excess of alkali, which is obstinately retained by the ppt. Boil till the ppt. is quite black. Allow to settle, decant through the filter, wash by decantation with boiling water and transfer to filter. Wash with boiling water till free from sulphate. Dry at 100°. Transfer as much of the ppt. as possible to a clock-glass placed on the glazed paper, and cover with a funnel. Burn the filter and transfer to the crucible. The oxide left on the filter has now been reduced to copper. It is moistened with a drop of strong nitric acid, carefully dried and heated. The main ppt. is now added and the whole ignited to constant weight.

(2) **As Cu_2S.**—The copper is pptd. as CuS, which is ignited to Cu_2S in a reducing atmosphere.

Weigh out as before. Dissolve in a conical flask of 400 c.cs. capacity in 100 c.cs. of water and 5 c.cs. pure sulphuric acid. The flask is fitted with a cork carrying two tubes, a delivery tube reaching to the bottom and an exit tube just passing through the cork. The solution is heated to boiling, the delivery tube attached to the H_2S Kipp, and the air swept out by a rapid stream of H_2S which has been washed with water. The exit tube is now closed with a piece of rubber tubing and a pinch-cock, and the flask is allowed to cool. Every five minutes it is gently shaken and the clip opened for a few moments to allow more H_2S to pass through. When it is quite cold pptn. will be complete.

It is filtered through a filter which is kept full of the liquid during the operation, or some of the moist sulphide will be oxidised to sulphate, thio-sulphate, etc., and will run through the filter. Remove any ppt. adhering to the delivery tube. The ppt. is finally washed with H_2S water till free from sulphuric acid (methyl orange) and dried at 100°. It is transferred to a weighed Rose crucible, the filter burnt completely and added to the crucible, a little *pure* sulphur added, and the crucible arranged as shown in Fig. 40. A stream of hydrogen from a Kipp is passed through, and the crucible is gently ignited, finally as strongly as possible with a bunsen. Allow to cool with the hydrogen still passing through, and do not remove to desiccator till nearly cold. Weigh as Cu_2S. Repeat the operation to constant weight.

(3) **As $Cu_2(CNS)_2$** (Rivot, *C.R.*, 38, p. 868).—The solution of copper sulphate as before is slightly acidified with hydrochloric acid. Oxidising agents must be absent. It is then treated with excess of freshly-prepared sulphurous acid and ammonium thio-cyanate added dropwise with constant stirring. The black cupric thio-cyanate first produced quickly turns white (cuprous). Allow to settle completely. Filter through a tared filter. Wash with cold water till free from excess of thio-cyanate (ferric chloride test). Dry at 110°

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in an air oven fitted with a thermo-regulator (Fig. 41) and weigh as described on p. 189. Repeat to constant weight.

Determination of sulphuric acid (Form : $BaSO_4$). *Use pure ammonium sulphate.*—This determination is one of the commonest estimations in chemistry and is one of the most difficult to carry out satisfactorily. The difficulties arise from the fact that $BaSO_4$ has very high adsorptive powers, and carries down with it, and obstinately retains, many other salts, especially the sulphates of iron, chromium, aluminium and potassium, and barium chloride and nitrate.

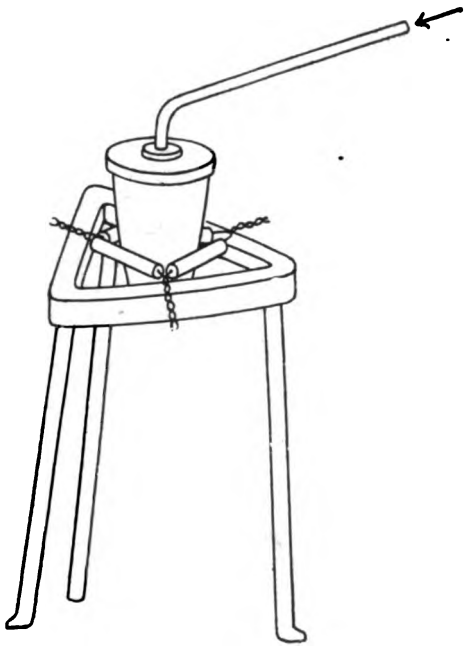

FIG. 40.

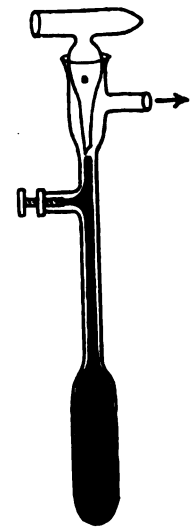

FIG. 41.

The solution therefore must be free from nitric acid and the trivalent metals, and potassium if possible. (For details as regards the treatment of these, see later under Sulphuric acid. At present we are concerned with the process itself.)

About 1·5 gms. of pure ammonium sulphate are weighed into a beaker, dissolved in 100 c.cs. of water and 20 c.cs. of 4N HCl added. Raise to boiling, and add dropwise (pouring it down the stirring rod) boiling barium chloride. In this way we avoid undue excess of barium chloride until the sulphate is pptd. and the ppt. is granular and filters well instead of being very fine and difficult to handle. When further addition of the reagent gives no ppt., allow to settle, decant through the filter, wash with boiling water, transfer to filter and wash with boiling water till free from barium (dilute sulphuric acid test). Dry at 100°, transfer ppt. as completely as possible to the crucible, burn filter and add to crucible, and ignite *gently* to constant weight. The

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ppt. adhering to the filter will be partly reduced to sulphide, which will be reoxidised on ignition. Or it may be treated with two drops of a mixture of sulphuric acid and alcohol (1 : 2) which converts the sulphide to $Ba(C_2H_5SO_4)_2$, which when dried carefully and ignited turns to sulphate. In case *very* accurate work is desired, Fresenius recommends digesting the dried and ignited ppt. with hot hydrochloric acid, evaporating and extracting with water. This may be done in the crucible, the ppt. after addition of water being again filtered, washed, dried and ignited as before. (Two filter ashes.)

Calculate percentage of SO_3 or SO_4 as desired.

Determination of hydrochloric acid (Form : AgCl). *Use pure sodium chloride.*—Weigh out about 0·5 gms. of the salt, dissolve in 75 c.cs. of water, acidify with pure nitric acid and add silver nitrate gradually with stirring as long as a ppt. forms. Just boil, allow to cool, filter through a Gooch crucible, wash with water acidified with nitric acid till free from silver (test with hydrochloric acid) and dry at 130° to constant weight.

A filter may be used, but on burning it the adhering ppt. is reduced to silver. (Unless care is taken this will alloy with the platinum wire.) Transfer to crucible; add 2 drops of nitric acid, warm gently, and then 2 drops of hydrochloric acid. Evaporate, and heat till the ppt. just melts. Cool in desiccator and weigh.

Calculate percentage of chlorine in the salt taken.

Hydrobromic acid and hydriodic acid are similarly estimated.

The silver halides readily carry down with them basic chlorides of heavy metals, especially on boiling. If these are present they must be removed. (See under Silver.)

Determination of phosphoric acid (Forms : $Mg_2P_2O_7$; $24MoO_3$, P_2O_5 ;) *Use selected crystals of sodium hydrogen phosphate Na_2HPO_4, $12H_2O$.*

(1) **As $Mg_2P_2O_7$.**—This method is applicable only to ortho-phosphates. Weigh out about 1·75 gms. of the crystals, which should be small and quite transparent, and dissolve in 100 c.cs. of water. Now add a slight excess of magnesia mixture * quickly, stirring all the time. Now add 50 c.cs. of strong ammonia and set aside overnight. The ppt. is $MgNH_4PO_4$, $6H_2O$. Filter, wash with cold dilute ammonia till free from chloride, and finally with ammonium nitrate solution. Dry and ignite to constant weight in the usual manner. Weigh as $Mg_2P_2O_7$.

N.B.—(1) Nebauer shows that if the pptn. is carried out in strongly ammoniacal solution the ppt. is contaminated with $Mg_3(PO_4)_2$, and if excess of ammonium salts are present, with $Mg(NH_4)_4(PO_4)_2$. The above procedure avoids this. (See also Gibbs, *Amer. Jour. Sci.* [3], 5, 114.)

(2) The filter is very reluctant to burn completely owing to the "fire-proofing" action of the phosphate. The last washing with ammonium nitrate is to assist this. If the ppt. looks black after ignition owing to unburnt carbon, it is re-ignited with the addition of a fragment of pure ammonium nitrate.

Alternatively, the ignition may be done in a Rose crucible in a stream of oxygen.

* Dissolve 60 gms. of magnesium chloride crystals and 85 gms. of ammonium chloride in 500 c.cs. of water. Dilute to a litre with 4N ammonia.

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Calculate the percentage of P_2O_5 in the salt taken.

(2) **As phosphomolybdic anhydride, $24MoO_3$, P_2O_5.**—The advantage of this method lies in the small percentage of phosphorus in the ppt. Hence an error in weighing the ppt. means a much smaller error in the weight of phosphorus. The pptn. is carried out by the method described by Woy, *Chem. Zeit.*, **21**, 442.

The reagents required are :

1. Nitric acid (1 vol. pure acid : 4 vols. water).
2. Ammonium molybdate (30 gms. per litre). (1 c.c. = 1 mgm. P_2O_5.)
3. Ammonium nitrate (340 gms. per litre).
4. 50 gms. of ammonium nitrate and 40 c.cs. of nitric acid in a litre of water, to use as wash liquid.

A quantity of the salt is weighed out containing *not more than* 0·1 gm. of P_2O_5. Dissolve in 50 c.cs. of water in a 500 c.c. beaker. Add 30 c.cs. of the ammonium nitrate solution and 15 c.cs. of the nitric acid. Heat to 80° C. Heat separately a very slight excess (in this case 125 c.cs.) of the molybdate solution to the same temperature. Pour slowly with stirring into the phosphate solution. Stir for a minute and set aside till nearly cold. Decant through a filter, wash by decantation with the wash liquid and dissolve in a very little dilute ammonia. Add to this 20 c.cs. of ammonium nitrate, 30 c.cs. of water and 1 c.c. of ammonium molybdate. Heat to 80° and reppt. by adding slowly, with stirring, 20 c.cs. of hot nitric acid.

The ppt., which is now pure

$$(NH_4)_3PO_4,\ 12MoO_3,\ 2HNO_3,\ H_2O,$$

is allowed to stand for 15 minutes, filtered through a Gooch crucible, dried at 100° and ignited in a larger nickel crucible as explained in Fig. 11. The bottom of the outer crucible should be gently heated at first, and finally to a dull red heat.

This method can be used to determine the phosphorus in iron. (See under Silicic acid.)

Determination of carbonic acid (Form : CO_2). *Use any pure carbonate.*—The acid is expelled as CO_2 from an apparatus that retains everything else, and the loss of weight found directly. Numerous pieces of apparatus are sold for this purpose, all on the same principle. That of Fresenius is described here, all the parts being ground together (see Fig. 42). A little water is placed in the flask, and some fairly strong sulphuric acid in the funnel. The absorption tube is filled with calcium chloride (over which CO_2 has been passed for a few minutes), which is held in place top and bottom by small plugs of glass-wool.

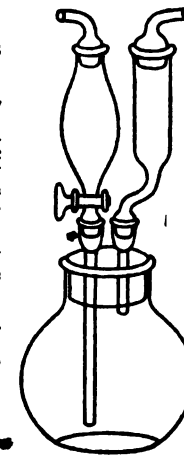

FIG. 42.

The apparatus is placed in the balance case for a few minutes and then weighed. The stopper of the flask is carefully removed, being held over the flask so that no water drops from the end of the funnel tube. About 1 gm. of the carbonate is introduced, the stopper replaced and the whole apparatus again weighed. The weight of substance taken is thus found. The funnel tap is now cautiously opened and a few drops of acid allowed to flow in. The

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reaction is thus carefully regulated. When all the carbonate is decomposed, any acid in the funnel is run into the flask, and the apparatus is placed on an asbestos wire gauze and heated gently until it *just* boils, meanwhile aspirating a slow current of air through the liquid. As soon as it boils remove the flame and allow to cool, continuing the gentle air current (not more than 2 bubbles a second). Finally replace in balance case and weigh.

Note.—The carbonate of magnesium (native) requires to be heated with the acid before action takes place.

The carbonates of barium, strontium and calcium require hydrochloric acid, and lead carbonate requires nitric acid, to dissolve them. There is danger of losing some of these acids on boiling, so in these cases the *upper* third of the absorption tube contains small fragments of pumice which have been soaked (in a vacuum) in saturated copper sulphate solution and heated for some time to 200° in an air oven. The anhydrous salt retains traces of acid which may come over.

Cases arise where CO_2 has to be estimated in presence of other volatile acids, *e.g.*

(1) Bleaching powder, where chlorine also comes off. In this case the two gases are evolved from the weighed substance by treatment with HCl in a small decomposition flask (or in the previous apparatus) and led into a 20 % solution of calcium chloride containing strong ammonia. Air, free from CO_2, is aspirated through the apparatus as in the previous description.

$$2NH_4OH + CO_2 = (NH_4)_2CO_3 + H_2O$$
$$(NH_4)_2CO_3 + CaCl_2 = CaCO_3 + 2NH_4Cl$$
$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

The pptd. $CaCO_3$ is filtered and washed and the CO_2 determined as in the previous method.

(2) Vat waste, soda ash, etc., where H_2S, SO_2, etc., may be evolved also. In this case the substance is treated with excess of alkaline hydrogen peroxide (use ammonia free from carbonate). Boil till excess of H_2O_2 is destroyed, and then determine the carbonate as before.

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CHAPTER III.

SYSTEMATIC STUDY OF THE ESTIMATION AND SEPARATION OF THE BASES.

METALS OF GROUP I.

Silver (Form : AgCl).—Ppt. with excess of dilute HCl and treat ppt. as already described, p. 196.

In case stannic and ferric salts are present, the solution must *not* be boiled or insoluble basic salts will be formed. Enough nitric acid must be present to prevent this, and the pptn. is performed entirely in the cold. The ppt. is caused to coagulate by shaking or stirring vigorously.

See also **Volumetric methods.**

Lead (Forms : $PbSO_4$; PbO).

1. **As $PbSO_4$.**—The solution of the lead salt (which should be free from salts of barium, strontium and calcium), and contain about 0·75 gm. of the salt in 80 c.cs. of water, is treated with a moderate excess of dilute sulphuric acid. Now add alcohol (industrial methylated spirit distilled from soda will do, but *not* ordinary methylated spirit) equal to about one-third of the volume of liquid ; filter, wash with alcohol till *quite free* from sulphuric acid (methyl orange test). Dry at 100°. Transfer ppt. as completely as possible to a watch-glass and cover with a funnel. Burn the filter. Treat the ash and reduced lead in the crucible with a little dilute nitric acid till dissolved, then a drop of sulphuric acid. Dry carefully, add the main portion of the ppt. Place the crucible in a larger crucible in which it is held in place by an asbestos ring (Treadwell) (Fig. 43). Heat the outer crucible to full redness. Cool and weigh. Repeat to constant weight.

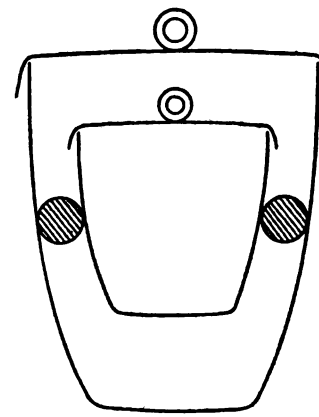

FIG. 43.

Note.—(*a*) Many substances can be transformed into sulphates and heated thus, the temperature being just insufficient to decompose them.

(*b*) If the lead is originally present as chloride or nitrate, the addition of sulphuric acid sets free hydrochloric or nitric acid in which lead sulphate is

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fairly soluble. In this case the salt is weighed into a porcelain basin, treated with a moderate excess of dilute sulphuric acid and evaporated, very slowly at first, on a sand-bath, until dense fumes of sulphuric acid come off. Allow to cool, transfer to a beaker, dilute with water and then with alcohol. Carry on as above.

2. **As PbO.**—Ppt. the lead solution (which must be free from other bases except sodium and potassium) with the slightest possible excess of ammonium carbonate solution, followed by very little ammonia.

Filter, wash free from ammonia (litmus paper). Dry at 100°.

Treat ppt. as described under $PbSO_4$, but do not add sulphuric acid to the crucible. The nitrate formed will turn to oxide on ignition.

Owing to the solubility of lead carbonate in ammonium salts, these must be absent, and the least possible excess of the reagent used.

Mercury (Forms: Hg_2Cl_2; HgS; Hg).

(1) **As Hg_2Cl_2.**—The mercur*ous* solution, free from silver and lead, is pptd. with sodium chloride solution, diluted, filtered through a Gooch crucible, dried at 100° and weighed.

Note.—Mercur*ic* solutions may be thus estimated if first reduced, in the presence of HCl, by excess of phosphorous acid. The necessary mixture of these acids is obtained by treating phosphorus trichloride with water (H. Rose).

GROUP II.

DIVISION A. THIO-BASES.

Mercury(*ic*).

(2) **As HgS.**—This method may only be used when the solution is free from oxidising agents, especially nitric acid, or much free acid. The pptn. is similar to that of copper sulphide except that it is carried out in the cold. Filter through tared filter or Gooch crucible, and dry at 105° to constant weight.

The presence of free acid, especially nitric acid, causes the formation of thio-basic salts, *e.g.* $Hg_2S(NO_3)_2$, which are not completely converted to sulphide. Unfortunately the usual estimations of mercury (in amalgams, cinnabar, etc.) are in solutions strongly acid with nitric acid. Boiling with hydrochloric acid causes loss of mercury chloride with the steam. Hence either reduce to mercurous state as above (Rose's method), or carry out the pptn. of the sulphide in *alkaline* solution according to **Volhard.**

The acid solution is nearly neutralised with sodium carbonate and treated with freshly-prepared sodium sulphide solution, added slowly, with constant stirring, till in excess. Finally heat to boiling, and continue adding the sodium sulphide till the ppt. has dissolved. $Hg(SNa)_2$ is formed, and is now decomposed by boiling with ammonium nitrate till all ammonia is expelled. Filter through a Gooch crucible, wash with hot water till free from sulphide (sodium plumbite test) and treat as above. When dry, extract several times with pure carbon disulphide, to remove any free sulphur, and repeat to constant weight.

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(3) **As metal** (Erdmann and Jannasch, *Jour. f. Pr. Chem.*, **31**, 385).—All compounds of mercury except the iodide are completely decomposed by heating with quicklime.

A glass combustion tube about 40 cms. long is drawn out at one end and bent at right angles as shown in Fig. 44. A plug of dry asbestos wool is pushed down nearly to the constriction, then a layer of quicklime about 25 cms. long. About 2 gms. of the substance is weighed out into a glass mortar containing 5 gms. of powdered quicklime, intimately mixed by means of a stout platinum wire and transferred to the tube by a funnel of glazed paper. The mortar is washed out with several small quantities of quicklime, which are also transferred to the tube. Finally a layer of 5 cms. of quicklime is put in, another small asbestos plug, and a cork carrying a short straight tube.

FIG. 44.

The drawn-out end is attached to a weighed Volhard absorption tube, the wider end of which is loosely filled with gold leaf.

The tube being placed in the furnace, first the long layer of lime is heated, then the short layer, and finally the mixture of lime and substance, whilst a *gentle* stream of carbon dioxide or coal-gas is passed through the apparatus.

The layer of quicklime, and the layer of the mixture should not be tightly packed or the gas will not pass through. If small granular quicklime is not available, the tube should, after being filled, be tapped gently in a horizontal position so as to cause a *small* channel to be left by the settling of the particles.

After the experiment conduct dry air through the Volhard tube to carry off moisture and weigh it. The mercury which invariably collects in the drawn-out portion of the tube is weighed by cutting off this portion, weighing it, heating to volatilise the mercury and weighing again.

Copper.—See p. 194.

Bismuth. As Bi_2S_3.—The solution should be only slightly acid with hydrochloric acid. Oxidising agents to be absent.

Saturate with H_2S as described under copper, p. 194, filter through Gooch crucible, wash with H_2S water, dry and remove sulphur as described under mercury, p. 200, or it may, without drying, be washed with alcohol, then carbon disulphide, then alcohol, finally ether and dried at 100°.

Bismuth nitrate must be pptd. as basic carbonate by ammonium carbonate. The diluted solution (disregard turbidity due to basic salt) is treated with a slight excess of the reagent, boiled, filtered and ignited to Bi_2O_3, the reduced bismuth being reoxidised as under copper (p. 194).

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Cadmium. As $CdSO_4$.—(1) *Other bases absent, and the cadmium present with a volatile acid.*—Treat in a weighed porcelain crucible with excess of dilute sulphuric acid. Evaporate very gently to dryness, and finally heat in a larger crucible as described under lead sulphate, p. 199.

(2) *Other bases are present.* (Except Group II.)—The sulphide is pptd. exactly as described under copper (p. 194) with the addition of 5 c.cs. of pure sulphuric acid for every 100 c.cs. of solution. Wash with hydrogen sulphide water, filter and dry as usual, transfer to a crucible and replace filter in funnel. Pour a little hot, strong hydrochloric acid through the filter to dissolve the ppt. adhering thereto, and allow it to run into the crucible. Repeat two or three times, using the absolute minimum of acid. Finally evaporate the acid in the crucible, thereby converting the sulphide to chloride. Now convert to the sulphate as described above and weigh as such.

Note.—It is not sufficiently accurate to weigh the sulphide, as thio-basic salts are invariably present however the pptn. is carried out (Treadwell).

DIVISION B. THIO-ACIDS.

Arsenic (ous). As As_2S_3.—The solution must be quite free from oxidising agents and the whole of the arsenic present in the arsenious state. The warm solution, acid with hydrochloric acid, is saturated with hydrogen sulphide as described on p. 194. Filter through a tared filter or Gooch crucible, dry at 100°, extract with pure carbon disulphide, dry again and weigh.

Arsenic (ic). As $Mg_2As_2O_7$.—The arsenic may be oxidised if necessary by warming with hydrogen peroxide and ammonia. 10 c.cs. of 4N ammonium chloride are then added for every 50 c.cs. of solution, and magnesia mixture, added dropwise, is well stirred in till pptn. is complete. Strong ammonia is then added and the mixture stood aside overnight. Filter through a Gooch crucible, wash with dilute ammonia, finally with ammonium nitrate solution, dry at 100° and heat in a larger crucible as described under lead sulphate (p. 199).

Note.—The ammonium nitrate is to destroy traces of carbon left by organic bases present in the ammonia. A filter cannot be used, as its combustion will reduce the arsenic causing loss by volatilisation.

Antimony. As Sb_2S_3.—The solution is treated with 2 or 3 grams of tartaric acid and very little hydrochloric. (If too much mineral acid is present pptn. will be incomplete.) Dilute to 150 c.cs. with water. The tartaric acid is to prevent pptn. of basic salts when this necessary dilution is performed. Saturate with hydrogen sulphide as on p. 194, filter through a Gooch crucible, wash with hydrogen sulphide water, alcohol, carbon disulphide, alcohol and dry at 100°.

Owing to the fact that Sb_2S_3 obstinately retains water, it is now necessary to heat to 230° for 20 minutes in a stream of carbon dioxide (to prevent oxidation). This is best done in a Paul crucible oven, Fig. 45. (See *Zeit. f. anal. Chem.*, **31**, 540.) Repeat to constant weight, but do not heat for longer than 15-20 minutes at a time.

Failing a Paul oven, the ppt. may be treated thus:

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After drying at 100° and weighing, a *weighed portion* is transferred to a weighed porcelain boat, placed in a combustion tube, and heated very gently in a stream of carbon dioxide. The temperature should not exceed 230°. From the loss of weight it is a simple matter to calculate the amount of impurity present in the *whole* ppt.

Tin. As SnO_2.—(1) If an alloy of tin is being examined, about 0·5 gm. is treated in a beaker with as little warm nitric acid (2 : 1) as is necessary. The beaker is covered with a clock-glass and gently warmed. When the action is completed, dilute with 100 c.cs. of boiling water and allow ppt. to settle. Filter, wash, dry and treat exactly as described under copper oxide, p. 194. Complete ignition over blowpipe to constant weight.

Note.—Antimony must not be present when this method is used.

(2) If tin is present as a soluble salt free from organic matter it is oxidised to the stannic state by bromine water, neutralised with ammonia, and stannic acid pptd. by diluting, adding ammonium nitrate and boiling. Treat ppt. as in (1).

(3) Alternatively, and in any case if organic matter is present, ppt. as sulphide in the presence of *very little* free acid. (The state of oxidation of the tin is immaterial.)

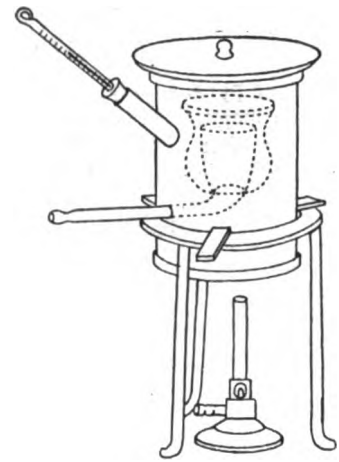

FIG. 45.

Filter, wash with ammonium nitrate (to prevent hydrosol formation), burn the filter and treat the metallic tin as described under copper, p. 194, in a Rose crucible. Now add the main ppt. and ignite in a stream of oxygen to constant weight. Weigh as SnO_2.

Note.—Tin sulphide obstinately retains sulphuric acid. If this was present, remove by adding a tiny fragment of ammonium carbonate before igniting (Treadwell). Repeat to constant weight.

Separation of Group II. from the remaining Groups.

This is carried out as described in Qualitative Analysis, Table A. It is most important to have the right amount of acid present. If too much is present, then tin, antimony and copper will be incompletely pptd. If too little, the ppt. will be contaminated with Group III. B. metals, especially zinc.

As a guide, about 15 c.cs. of 4N acid to 100 c.cs. of the solution will be found correct. (This is a maximum.)

Group II. A. is separated from Group II. B. by the use of *sodium* sulphide (freshly made), except when mercury is present, in which case ammonium sulphide should be used.

For further particulars see Chapter IV.

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GROUP III.

DIVISION A.

Iron, chromium and aluminium have been discussed in Chapter II.

Uranium. As UO_2.—The metal is pptd. from solution (which must be free from carbonates and ammonium carbonate; see Book II. under Uranium) as ammonium uranate, $(NH_4)_2U_2O_7$. Filter, wash, dry, transfer to a Rose crucible in the usual way, ignite very gently in air and finally strongly in a stream of hydrogen.

Separation of Group III. A. from the remaining Groups.

The pptn. is carried out as described in Book II., Table A. If, however, much magnesium is present the ppt. will certainly be contaminated with it. Hence after filtering, the ppt. in this case should be redissolved in dilute hydrochloric acid and repptd. The two filtrates and the washings are of course united.

The same remarks apply especially to the alloys of aluminium (duralumin, magnalium, etc.). The pptn. of the aluminium in such alloys as contain metals of the succeeding groups must always be carried out twice.

GROUP III. B.

Zinc (Forms : ZnO; ZnS).

(1) **As ZnO.**—No other bases except sodium and potassium may be present.

Ppt. as carbonate by adding pure sodium carbonate solution dropwise to the boiling neutral liquid. To prevent adsorption of the alkali use the least possible excess. Filter hot, dry at 100°, transfer the ppt. to the crucible and moisten the filter with ammonium nitrate solution. Dry again and incinerate. Transfer the ash to the crucible and ignite to oxide, avoiding the entrance into the crucible of reducing gases from the flame, or the oxide will be reduced to zinc and volatilised. (The ammonium nitrate is to prevent such reduction by the burning filter.)

A muffle furnace should therefore be used for the ignition if available.

Note.—If sulphuric acid is present, basic sulphate will contaminate the ppt. In this case, and in case other metals (except Groups II. and III.) are present, employ method (2).

(2) **As ZnS.**—Render just alkaline with sodium carbonate. Redissolve the ppt. with acetic acid and add a few c.cs. of ammonium acetate solution (saturated). Ppt. with *colourless* ammonium sulphide (or hydrogen sulphide). Allow to settle completely, filter, wash with dilute ammonium acetate and ammonium sulphide solution, dry, transfer to Rose crucible, treat the filter as in method (1) and add to the crucible. Cover with *pure* sulphur and ignite gently in a stream of hydrogen. Repeat to constant weight.

Manganese (Forms : Mn_3O_4 ; MnS ; $MnSO_4$).

(1) **As Mn_3O_4.**—No other bases except the alkalis may be present.

Ppt. the carbonate as described under zinc, (1), but with *ammonium*

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carbonate. Filter, wash and ignite wet, with free access of air (muffle best) to constant weight.

(2) **As MnS.**—Ppt. as described under copper sulphide, in presence of excess of ammonium chloride and not too much ammonia. Saturate *cold* with hydrogen sulphide. The ppt. is finely divided, and requires special filter paper to retain it. Wash with dilute ammonium sulphide. Treat as with zinc sulphide, except that ammonium nitrate is unnecessary.

Note.—The pptn. in the cold is only necessary in the presence of alkaline earths or magnesium. These absent, it may be done at the boil, when the ppt. settles much better.

(3) **$MnSO_4$.**—The carbonate, oxides and sulphides may all be converted to the sulphate as described under cadmium, p. 202. Similarly manganese combined with a volatile acid and in absence of other bases may be so determined.

Manganates and permanganates.—Reduce to manganese salts by passing sulphur dioxide into the acid solution. Then use one of the above methods.

Nickel. As metal.—Only alkalis may be present besides the nickel. The solution is pptd. with KOH as described under copper, p. 194. When pptn. is complete, bromine water is added until the ppt. is converted into $Ni(OH)_3$, which settles and filters much better than $Ni(OH)_2$. Transfer the filtered and washed ppt. to a Rose crucible, add the filter ash and reduce to nickel in a stream of hydrogen with the blowpipe flame. Cool in the hydrogen current and weigh.

Cobalt. As metal.—The operation and the conditions are the same as for nickel.

Separation of Group III. B. from Group IV. and Magnesium.

The *neutral* solution of the chlorides in a conical flask is treated with the necessary ammonium chloride and colourless ammonium sulphide added dropwise till in *slight* excess. The air in the flask is then displaced by a rapid stream of hydrogen sulphide, the flask closed whilst the gas is passing (clips on rubber tubing) and left overnight.

Filter and wash as under Zinc Sulphide.

Note—(1). The ammonia used for the preparation of the sulphide must be quite free from carbonate or Group IV. will contaminate the ppt.

(2) NiS forms a hydrosol in the presence of much ammonium sulphide, especially the yellow variety. Hence the reason for the exclusion of air and the use of the least possible excess of the reagent.

GROUP IV.

Barium (Forms : $BaSO_4$; $BaCrO_4$).

(1) **As $BaSO_4$.**—Lead and strontium, and the bases mentioned under sulphuric acid, p. 195, must be absent.

Treat the boiling solution with boiling dilute sulphuric acid added dropwise until in excess. Settle, filter, wash with hot water till free from sulphuric acid. Ignite wet, or in the usual way. Do *not* use the blowpipe. (See p. 196.)

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(2) **As $BaCrO_4$.**—Lead and mercury must be absent. The solution is acid with *acetic* acid only and the pptn. is made with ammonium chromate if available, otherwise with the potassium salt. Filter through a Gooch crucible and treat as already described under chromic acid, p. 193.

Strontium. As $SrSO_4$.—The procedure is exactly as described under lead sulphate, p. 199.

Note.—$SrSO_4$ is appreciably soluble in nitric and hydrochloric acids and in magnesium and alkali chlorides.

Calcium (as CaO).—The calcium is pptd. as oxalate from solution slightly alkaline with ammonia. No other base but magnesium and the alkalis may be present. The solution should be boiling, and boiling ammonium oxalate is added dropwise till present in excess. Filter, wash with hot water, ignite wet or in the usual way, finally over the blowpipe or in a muffle to constant weight. During cooling the crucible should be placed in a desiccator containing soda-lime, to prevent absorption of carbon dioxide.

If much magnesium be present, see next paragraph.

Separation of Group IV. from Group V.

The three alkaline earths are pptd. as oxalates from *dilute* solution containing ammonium chloride and just alkaline with ammonia. Carry out exactly as described under calcium. Excess of ammonium oxalate is an advantage.

If much magnesium is present (*e.g.* dolomite) a single pptn. is insufficient; the ppt. will surely contain magnesium oxalate. It must therefore be dissolved in hydrochloric acid and again rendered alkaline with ammonia and repptd.

GROUP V.

Magnesium. As $Mg_2P_2O_7$. (Gibbs, *Amer. Jour. Sci.* [3] **5**, 114.)—The magnesium is pptd. by adding dropwise, to the boiling liquid, a solution of microcosmic salt, till no further ppt. forms. The magnesium is pptd. as $MgHPO_4$. On cooling and slowly adding ammonia with constant stirring, the ppt. is converted to $MgNH_4PO_4, 6H_2O$. Filter, wash, dry and ignite as already described under phosphoric acid, p. 196.

Potassium (Forms: $KClO_4$; K_2PtCl_6; K_2SO_4).

(1) **As $KClO_4$.**—This method is by general consent regarded as the cheapest, simplest and best method of determining potassium. With other methods, no base except sodium may be present, and the salt *must* be the chloride. Sir W. Crookes states that the perchlorate method gives accurate results in the presence of the alkaline earths, magnesium, sodium, iron, aluminium, sulphates and phosphates. (See also *Amer. Jour. Sci.*, June, 1895.)

The substance in which the potassium is to be determined (*best* as the chloride) is dissolved in a little water, treated with perchloric acid of S.G. 1·42 and evaporated to a small volume on the water-bath. 95 % alcohol containing a little perchloric acid is added, the ppt. transferred to a tared filter or a Gooch crucible, washed with 95 % alcohol, dried at 100° and weighed as $KClO_4$.

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The separation from sodium, involved in almost all determinations of potassium, is properly accomplished by this method.

(2) **As K_2PtCl_6.**—The potassium *must* be present as chloride and no other base but sodium may be present.

If the potassium and sodium are *not* present as chlorides, they must, after weighing, be converted thereto by evaporation with strong hydrochloric acid if a volatile acid is present, or by *exact* pptn. with barium chloride in the case of sulphate or ferric chloride in case of phosphate.

The solution of the two chlorides in water is treated with a slight excess * of chlorplatinic acid and evaporated dry on the water-bath. The residue is treated with a little absolute alcohol, well stirred, brought on to a tared filter moistened with absolute alcohol and washed with alcohol until the washings are colourless. (The sodium salt is soluble in alcohol.) Dry at 100° and weigh as K_2PtCl_6.

The authors of the correct working out of this method (*Chem. News*, xvii. 244) take 488·4 as the molecular weight of K_2PtCl_6. This makes use of the old atomic weight for platinum (197·20), whereas the accepted atomic weight is 195·2. In spite of this the results are more accurate when the older number is employed.

According to Treadwell, this is due to the fact that the ppt. is not pure K_2PtCl_6, but contains also a little hydrogen and oxygen, due to slight hydrolysis.

(3) **As K_2SO_4.**—Used where potassium is the only base present except ammonium, and is combined with a volatile or an organic acid.

Ammonium salts if present are destroyed by very gentle ignition, the residue is dissolved in a little water and transferred to a crucible. It is evaporated dry on a water-bath, allowed to cool and moistened with strong sulphuric acid. Evaporate dry on water-bath and then heat to barely visible redness with addition of a fragment of pure ammonium carbonate. Repeat to constant weight.

Sodium. As Na_2SO_4.—Procedure and conditions the same as for potassium. In a mixture of sodium and potassium chlorides it is usual to weigh them, determine the potassium and estimate the sodium by difference.

Lithium. As Li_2SO_4.—Conditions and procedure as for potassium.

Ammonium. As $(NH_4)_2PtCl_6$, converted to Pt.—Conditions and procedure as for potassium, which must of course be absent. The final ppt., however, is ignited in the usual manner in a porcelain crucible (gently at first, finally with free access of air) and the residue of platinum weighed. $Pt = 2NH_4$.

Ammonium is best determined volumetrically, q.v.

TREATMENT OF INSOLUBLE BODIES.

Sulphates of lead and strontium are converted to carbonates by boiling with excess of sodium carbonate for an hour, filtering, washing with dilute sodium carbonate till free from sulphate, then with water and dissolving in dilute nitric or hydrochloric acid. Carry on as usual.

* The amount to be added is roughly calculated by assuming that the whole weight of the chlorides is NaCl. This ensures a suitable excess.

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Barium sulphate must be fused in a platinum crucible with 6 times its weight of fusion mixture. The fusion after cooling is dissolved in a little cold water, brought on to a filter, washed with cold sodium carbonate solution till free from sulphate. Carry on as with strontium.

Stannic anhydride (tinstone) is fused in a platinum crucible with 4 times its weight of KHF_2 (Hallett). The mineral must be in a very fine powder. After the action is complete the crucible is allowed to cool, treated with sulphuric acid and warmed gently to expel hydrofluoric acid, and treated with a little cold water and filtered. On boiling the filtrate stannic acid is pptd.

Alumina is fused with $KHSO_4$, the melt dissolved in water and the aluminium pptd. as hydroxide.

For treatment of *insoluble silicates*, see end of Chapter IV.

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CHAPTER IV.

SEPARATIONS.

GROUP I.

Silver from lead (*Benedict and Gaus*).—The solution of the nitrates is pptd. with potassium iodide. Sufficient nitric acid (1 : 1) is then added and the liquid boiled till the lead iodide is destroyed and the iodine volatilised. Filter through a Gooch crucible, dry the silver iodide at 110° and ppt. the lead as sulphate from the filtrate.

Note.—(1) This is not available in the presence of mercury, as silver iodide is soluble in solutions of mercury nitrate.

(2) Silver may be separated from all other metals except lead by pptn. with hydrochloric acid. If mercury is present it is oxidised by nitric.

Lead from mercury.—Ppt. the lead as sulphate. The alcohol is evaporated from the filtrate and the mercury determined by Rose's method, p. 200.

GROUP II. A.

Bismuth from lead (*Jannasch*).—Ppt. the sulphides. After drying place them, with the filter ash, in a porcelain boat which is put into a combustion tube about 25 cms. long, one end of which is drawn out and bent at right angles. This end dips into a flask containing dilute nitric acid (1 : 2). Dry bromine vapour (carried over by a current of dry CO_2 passing through a wash-bottle containing bromine, which is again dried by passing through a U-tube containing glass-beads moistened with sulphuric acid) is led through the tube, and the boat is gently heated with a small flame. The metals are converted into bromides and the $BiBr_3$ readily volatilises and is caught in the nitric acid. The flask should be fitted with an exit tube to which an absorption flask containing alcohol is attached, to absorb excess of bromine. The heating should not be carried beyond the point at which the lead bromide begins to melt. Distil the sublimate as completely as possible into the receiver.

If no other metals are present, the lead may be calculated from the weight of lead bromide left in the boat, or it may be dissolved in chlorine water and determined as sulphate.

The bismuth solution is filtered from sulphur, evaporated to a small volume and the bismuth determined by pptn. with ammonium carbonate as on p. 201.

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Bismuth from cadmium.—Exactly as bismuth from lead.

Mercury from any of the thio-bases.—The sulphides are pptd., filtered and washed; a hole is made in the filter and the sulphides washed into a beaker by a stream of boiling water. The liquid is boiled and hot nitric acid (1 : 1) is added, *one drop at a time*, till no further action takes place. If necessary the filter may also be treated with hot *dilute* nitric acid, but this is not generally necessary.

The mercury is left as an insoluble thio-basic nitrate; the other metals are converted to nitrates. Dissolve the residue in aqua regia and estimate the mercury by Rose's method, p. 200.

Note.—If the method is carried out as described, lead will *not* be converted into sulphate and the separation will be complete.

Alloys of the thio-bases with tin (solder, pewter, etc.).—The alloy is treated with nitric acid as already described, and the tin determined as SnO_2, p. 203. Antimony must not be present.

In the case of **bronzes (Cu-Sn alloys)** a little phosphorus is usually present. This is determined in a separate portion as phosphoric acid. It will be obtained with the SnO_2 as P_2O_5. The weight of P_2O_5 found must therefore be subtracted from this to obtain the weight of SnO_2.

The phosphorus is determined thus (Oettel, *Chem. Zeit.*, 1896, 19):

About 5 gms. of the alloy are treated with nitric acid, the ppt. of metastannic acid and phosphoric acid filtered, washed, dried and transferred to a porcelain crucible, the filter ash being also added. Ignite, cool, add some solid potassium cyanide and fuse. The tin is reduced to a button of metal, the P_2O_5 forms potassium phosphate. Cool, dissolve in water and filter, destroy the cyanide by boiling with dilute hydrochloric acid *in the draught-cupboard*, and determine the phosphorus as $Mg_2P_2O_7$.

GROUP II. B.

Separation of arsenic, antimony and tin (Fischer and Classen, *Ber.* xviii. p. 1110).—The metallic sulphides (repptd. if necessary, for separation purposes, from the ammonium sulphide solution) are dissolved in a large covered beaker in alkaline hydrogen peroxide. Sodium arsenate, antimonate and stannate are thereby formed. Boil to destroy excess of hydrogen peroxide, concentrate on a water-bath, and transfer to a 500 c.c. distilling flask, by means of a thistle funnel. Rinse the vessel out with strong hydrochloric acid, add the washings to the flask, mix with 25 gms. of ferrous ammonium sulphate (to reduce to the *-ous* state) and make up to about 180 c.cs. with strong hydrochloric acid. By means of an adapter the flask is now fitted to a conical flask as a receiver, containing 400 c.cs. of water, and immersed in a large bowl of water to keep it cool. (The distillation flask should now be in an inclined position.) Into the distilling flask a rapid stream of hydrochloric acid gas is now passed for an hour, and the liquid is then distilled down to 50 c.cs., keeping up the stream of gas. The arsenic passes over as trichloride, and is determined in the distillate as sulphide or volumetrically. The solution in the flask is diluted considerably, the sulphides pptd. by hydrogen sulphide. The separation is best effected electrolytically, but it may be carried out by

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Hampe's method (*Chem. Zeit.*, 18, 1900). After filtering and washing they are dissolved in warm freshly-made sodium sulphide, and sodium peroxide added a little at a time till the colour of the liquid is discharged and oxygen comes off. Now add one-third of the volume of 90 % alcohol, filter off the sodium metantimonate, wash it with alcohol, dissolve in hydrochloric and tartaric acids, and ppt. by hydrogen sulphide in the usual way. The tin in the filtrate is determined by evaporating the alcohol on a water-bath, just acidifying with dilute sulphuric acid and saturating with hydrogen sulphide. Weigh as SnO_2 as already described on p. 203.

Note.—Alloys seldom contain arsenic. Antimony and tin, however, are frequently met with. Separate by the latter portion of the above method, or electrolytically.

GROUP III. A.

Iron from aluminium.—(1) The solution of the chlorides (iron in ferric state) is added to pure 2N caustic soda in a silver basin (porcelain may be used). If the iron is in the ferrous state, some hydrogen peroxide should be added to the soda. The solution should finally be strongly alkaline. Boil, dilute with hot water, filter and wash free from alkali. Determine the aluminium in the filtrate and washings by acidifying with nitric acid and pptg. as $Al(OH)_3$. The iron ppt., which will be contaminated with alkali, is dissolved in dilute hydrochloric acid and pptd. by ammonia.

(2) A far quicker and better way is to ppt. both metals by ammonia, ignite, weigh and fuse with $KHSO_4$. The fusion is maintained for about 2 hours. The melt should dissolve clear in water. Wash the crucible and lid thoroughly and add the washings to the solution. Make up to a known volume, reduce the iron and determine it volumetrically as on p. 248, and find the alumina by difference.

Iron from chromium.—The solution of the chlorides is poured into a warm solution of caustic soda and hydrogen peroxide in a silver basin. Boil, dilute, filter and wash free from chromate. Reppt. the iron as above. Acidify the filtrate with acetic acid and ppt. as barium chromate as on p. 193.

Note.—If sulphuric acid is present the chromate must be reduced again by boiling with alcohol and hydrochloric acid and pptg. the hydroxide as on p. 193.

Chromium from manganese (v. Knorre, *Zeit. Anal. Ch.*, 1904, [1] 43.—The solution, free from iron, is rendered acid with acetic acid by almost neutralising with ammonia (if acid) and then adding ammonium acetate. The mixture is now treated with some excess of ammonium persulphate, when the manganese is pptd. as MnO_2 and the chromium converted to chromate. Carry on as usual.

Chromium from aluminium.—If the filtrate from the iron-chromium separation contains aluminium, acidify with *nitric* acid and ppt. the aluminium as hydroxide. The filtrate is rendered acid with acetic acid before pptg. as barium chromate.

Titanium from iron and aluminium.—In analysing rocks the iron ppt. almost always contains titanium as $TiO(OH)_2$. The mixed ppt. (Group III. A.)

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is dried and fused with excess of fusion mixture in a platinum crucible. The crucible is dipped into cold water whilst still hot (so that no water enters) and the melt is thus readily detached. It is extracted with cold water and filtered. The ferric oxide after washing is dried, the filter burnt and the whole dissolved in hot strong hydrochloric acid and the iron pptd. in the usual way.

The filtrate contains sodium aluminate and titanate. Render just acid with hydrochloric acid, add some acetic and sulphuric acid and boil for 3 hours by passing in steam (this avoids evaporation). The ppt. of meta-titanic acid, $TiO(OH)_2$ is filtered, washed and ignited wet. Weigh as TiO_2. The aluminium in the filtrate is determined in the usual way.

Iron from manganese (*Spiegel-eisen, etc.*).—Group III. A. ppt. is always contaminated with manganese if that metal is present. The separation is carried out by one of the following methods:

(1) **Basic acetate method.**—The ppt. of ferric hydroxide containing some $MnO(OH)_2$ is dissolved in hydrochloric acid, boiled till chlorine is expelled and the concentrated solution transferred to a large beaker. Not more than 0·5 gm. of iron should be present. In order to have the least possible excess of acid present it is treated with sodium carbonate till a permanent ppt. just forms and this is redissolved by the addition of a few drops of hydrochloric acid. Now add 5 c.cs. of a saturated solution of ammonium acetate, dilute to 500 c.cs. with boiling water, and boil for 2 minutes. Filter whilst hot, dissolve the ppt. in hydrochloric acid and repeat.

The ppt. $= Fe(OH)_2(C_2H_3O_2)$ and the corresponding aluminium salt.

Dissolve in hydrochloric acid and carry on as previously described.

The *combined* filtrates and washings are acidified with 15 c.cs. of strong hydrochloric acid, evaporated to a syrup, diluted with water and the manganese pptd. by ammonium sulphide and determined as already described.

This manganese must of course be added to the main portion, which will be obtained in the usual way in Group III. B.

(2) **The succinate method.**—Group III. A. ppt. is dissolved in hydrochloric acid, evaporated and neutralised as before, diluted to 100 c.cs. and sodium succinate added. Filter and wash with cold water. The filtrate contains the manganese. The ppt. is iron succinate (basic) and aluminium, if that metal is present.

Treatment in the presence of phosphoric acid.—Neither of the methods described in "Qualitative Analysis" is sufficiently accurate for quantitative work in the presence of all bases, but the following cases may arise:

(1) **Group III. is absent.**—Employ the ferric chloride separation described on p. 167.

(2) **Group III. is present, except Cr and Al.**—Just acidify the solution with hydrochloric acid, add 3-5 gms. of tartaric acid, then a slight excess of colourless ammonium sulphide. The solution, which is contained in a conical flask of 200 c.cs. capacity, is now diluted nearly to the stopper of the flask with boiled and cooled water, corked up to prevent oxidation and set aside overnight.

The ppt. contains the *sulphides* of Group III., the filtrate the phosphoric acid.

The tartaric acid prevents the pptn. of ferric phosphate, but not of chromium and aluminium.

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(3) **Aluminium is present.**—Ppt. Group III. A. in the usual way, filter, wash, ignite and weigh the ppt. (Fe_2O_3, Al_2O_3, P_2O_5).

Determine the iron volumetrically after fusion with $KHSO_4$.

Determine the P_2O_5 in a *separate* portion by ppting. Group III. A., filtering, washing, dissolving the ppt. in nitric acid and finding the P_2O_5 by the molybdate method.

(4) **Any bases are present in filtrate from Group II.**—Ppt. the P_2O_5 by ammonium molybdate as described on p. 197.

Evaporate the filtrate with sulphuric acid till dense fumes of the vapour come off. Dilute, *after cooling*, with water (care !) and a little hydrochloric acid. Filter from any $BaSO_4$ or $SrSO_4$. Saturate with hydrogen sulphide in a small pressure flask, stopper it up and warm *gently* on a water-bath for several hours.

Ppt. = MoS_3. Filter and wash. Reject ppt. Carry on as usual with the filtrate.

GROUP III. B.

Separation of zinc from nickel, cobalt and manganese (Zimmermann, *Ann. Ch. Ph.*, 1880, 226).—Add sodium carbonate solution to the slightly acid solution of the four metals till a permanent ppt. just forms. This is *just* redissolved by adding dilute hydrochloric acid dropwise. Then add 8 drops of 4N hydrochloric acid and 10 c.cs. of 20 % ammonium thio-cyanate. This prevents the pptn. of nickel and cobalt sulphides and at the same time stops the formation of a zinc sulphide hydrosol. Now saturate with hydrogen sulphide at 70° C., cork up and stand overnight, filter off the zinc sulphide and wash with dilute ammonium thio-cyanate containing hydrogen sulphide. Determine the zinc sulphide as previously described.

The filtrate, freed from hydrogen sulphide by gently boiling and passing a current of carbon dioxide through the boiling liquid, is treated with sodium carbonate till a permanent ppt. forms. It is then strongly acidified with acetic acid and to each 100 c.cs., 5 c.cs. of saturated ammonium acetate are added. Heat to 70°, saturate with hydrogen sulphide and filter off the nickel and cobalt sulphides.

The manganese in the filtrate is determined by one of the methods already described. The nickel and cobalt are separated by Liebig's method as follows.

Nickel from Cobalt.

1. **Liebig's method.**—The ppt. sulphides are dissolved in the minimum of aqua regia on the filter (which is covered with a clock-glass). After thoroughly washing the solution into a basin, and rinsing the clock-glass also, evaporate it dry on a water-bath. Dissolve the residue in water and add a solution of pure potassium cyanide till the ppt. which first forms redissolves. Gently boil for a few minutes till the colour change is complete, treat with some excess of pure potash and then add bromine water till no more ppt. ($Ni(OH)_3$) falls. Boil. The solution should still be strongly alkaline. Dilute with cold water, filter and determine the nickel as metal.

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The potassium cobalticyanide in the filtrate and washings is concentrated as far as possible on the water-bath, and the residue treated with a little strong sulphuric acid, covered with a clock-glass and gently warmed till effervescence ceases. Then continue the heating till fumes of sulphuric acid come off. Cool and *carefully* dilute with water, rinse the clock-glass into the solution and ppt. the cobalt with alkali and bromine water in the usual way.

2. **Hallett's method** (*Eng. Min. J.*, 1913, 857). *Forms*: Nickel salt of α-dimethyl glyoxime, $NiC_8H_{14}N_4O_4$. Cobaltinitroso-β-naphthol.

The solution containing both nickel and cobalt, freed from metals of Groups II. and III. A. by the usual methods, and containing ammonium chloride, is boiled and treated with a 1 % solution of α-dimethyl glyoxime in 98 % alcohol till no further pptn. takes place. Render alkaline with ammonia, set aside for half an hour, filter through a Gooch crucible and wash with hot water containing a little ammonia. Dry at 115°-120° to constant weight and weigh as $NiC_8H_{14}N_4O_4$ containing 20·33 % of nickel.

Note.—α-diphenyl-glyoxime may be used, giving more accurate results. The product is $NiC_{28}H_{22}N_4O_4$ containing 10·93 % of nickel. Dry at 110°.

The filtrate and washings containing the cobalt are evaporated with sulphuric acid till thick white fumes come off. The organic matter is thus destroyed. Allow to cool, add dilute hydrochloric acid (care!) and warm till the solution is clear. At 50° C. add a warm solution of nitroso-β-naphthol in 50 % acetic acid till no more ppt. falls. Set aside on the hot-plate for an hour. Filter and wash with (*a*) dilute hydrochloric acid, (*b*) hot water. Ignite in the usual manner and weigh as Co_3O_4.

GROUP IV.

Separation of barium from strontium or calcium.—The barium is pptd. as $BaCrO_4$ from solutions acid with acetic acid. Ammonium chromate is the best precipitant, and may be made by adding ammonia to ammonium dichromate and boiling off any excess of ammonia. The solution should not be alkaline.

Separation of barium, strontium and calcium (Rawson, *Chem. News*, 1897, May 21st).—The nitrates of the three metals are evaporated dry on the water-bath and treated with strong nitric acid. Stir thoroughly, allow to settle and pour through a filter moistened with strong nitric acid. Repeat two or three times, and finally bring the residue on to the filter and wash with nitric acid till the washings no longer show the calcium flame.

The filtrate contains calcium nitrate. Evaporate on the water-bath and determine the calcium by conversion to sulphate.

The residue, consisting of barium and strontium nitrates, is dissolved in water, diluted considerably, rendered alkaline with ammonia and acid with acetic acid, and the barium determined as $BaCrO_4$. The strontium in the filtrate is determined as $SrSO_4$.

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GROUP V.

Magnesium is separated from the other members of the group by the method of its determination. It will usually be necessary to evaporate dry and drive off the excess of ammonium salts that have accumulated during the analysis, or the ppt. of $MgNH_4PO_4$, $6H_2O$ will be contaminated as already described on p. 196.

The separation of potassium has already been described, p. 206-7.

Lithium from sodium and potassium. *Rammelsberg's method, modified by Treadwell.*—The mixed chlorides are evaporated on the water-bath in a conical flask through which a current of air is passed. When dry the flask is heated to 140° in an oil-bath, meanwhile passing a current of dry hydrochloric acid gas. This finally dehydrates the mixture whilst preventing the formation of lithium hydroxide.

The residue is now treated with a mixture of alcohol and ether saturated with hydrochloric acid gas, and the flask stoppered and frequently shaken during 12 hours. Filter and wash the residue with ether-alcohol.

The filtrate contains lithium chloride. The residue is the remaining chlorides. Evaporate the filtrate, and convert the chloride to sulphate, in which form it is weighed.

Ammonium is always determined volumetrically with the original substance.

Treatment of insoluble bodies.—Substances likely to be met with are:

Bauxite, Al_2O_3, containing Fe_2O_3.

Chromite, FeO, Cr_2O_3.

Fluorspar, CaF_2.

Cryolite, Na_3AlF_6.

Many silicates, as felspar, mica, etc.

Clay, aluminium hydrogen silicate, usually containing iron and some alkalis.

All these substances must be reduced to a *very fine powder* in an agate mortar before weighing out.

Bauxite is fused with $KHSO_4$. The melt should dissolve clear in water, unless silica is present.

Chromite should be fused in a platinum crucible with six times its weight of a mixture of 5 parts of fusion mixture and 1 part of potassium nitrate. The melt is extracted with boiling water, and filtered from the ferric oxide, which is dissolved in strong hydrochloric acid.

The filtrate contains chromates of sodium and potassium. Cautiously acidify with acetic acid, filter if necessary and determine as $BaCrO_4$.

Fluorspar and cryolite may be converted to sulphates by gently heating with strong sulphuric acid. When all hydrofluoric acid is removed heat till thick fumes of sulphuric acid come off, allow to cool, *cautiously* dilute with water and hydrochloric acid, boil. Filter from any $BaSO_4$ and carry on in the usual manner.

Insoluble silicates are fused with six times their weight of fusion mixture in a platinum crucible. Extract the melt with water, *cautiously* acidify strongly with hydrochloric acid and evaporate dry on the water-bath. Moisten the

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residue thoroughly with strong hydrochloric acid, and dry again at 110°. Extract with cold water just acidified with hydrochloric acid, filter, wash and ignite the silica wet. Weigh as SiO_2. Carry on with the filtrate in the usual manner.

The alkalis in insoluble silicates obviously cannot be found by this method. The simplest and best method is that of Lawrence Smith.

About 0·5 gm. of the finely powdered mineral is mixed *intimately* in an agate mortar with 0·5 gm. of *pure resublimed* ammonium chloride and 3 gms. of *pure pptd.* calcium carbonate. Transfer this to a platinum crucible by means of a funnel of glazed paper and a feather or brush, and wash out the mortar with another gram of calcium carbonate, which is also transferred to the crucible. The covered crucible is now *very gently* heated till no more *ammonia* comes off. (No ammonium chloride fumes should be evolved, or the heat is too strong.) *Then gradually* raise the temperature till the lower half of the crucible is a dull red. The upper half should *not* be too hot. This temperature is maintained for an hour. Allow to cool. Extract with 80 c.cs. of water in a basin and warm gently till all the contents of the crucible *and lid* have been detached. Rinse the crucible and lid.

We have now the lime and silica in an insoluble form (also the other bases present), the alkalis as chloride, and some calcium chloride formed by the reaction. Filter and wash well. Reject the residue.

To the filtrate and washings in a basin add pure ammonium carbonate; evaporate (without filtering) to about 40 c.cs., add a little more ammonium carbonate and a few drops of ammonia and filter. Receive filtrate and washings in a weighed platinum basin, evaporate dry and heat *very gently* to drive off ammonium salts, finally heating *nearly* to redness. Allow to cool in a desiccator and weigh as *quickly as possible* (LiCl, if present, is very deliquescent).

Separate as already described.

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CHAPTER V.

DETERMINATION OF THE ACID RADICALS.

GROUP I.

THE determination of the halogen acids has been described in Chapter II.

Hydrocyanic acid. As AgCN.—Ppt. exactly as described for hydrochloric acid. Do not have the solution very strongly acid with nitric acid. Either weigh the ppt. on a tared filter after drying at 100°, or ignite to metallic silver (with free access of air).

Hydrosulphuric acid, H_2S. As $BaSO_4$.

(*a*) *As free* H_2S *or soluble alkali sulphide.*

(1) Oxidise by treatment with ammoniacal hydrogen peroxide. Heat slowly to boiling and ppt. the sulphate as $BaSO_4$ after acidification.

(2) Ppt. as CdS by adding cadmium acetate. Oxidise the CdS by strong nitric acid and boil well. Ppt. as $BaSO_4$.

(*b*) *As sulphide soluble in dilute acid.*

The H_2S is evolved in the apparatus shown in Fig. 46, and passed into ammoniacal hydrogen peroxide, contained in a Volhard absorption flask. Before adding acid, air is swept out of the flask by a stream of carbon dioxide. The tap is closed, the absorption tube connected up and the acid (hydrochloric) put into the funnel. After decomposition is complete just raise to a boil and sweep out all H_2S by a stream of CO_2. Ppt. as $BaSO_4$ after rinsing out the absorption tube and acidifying.

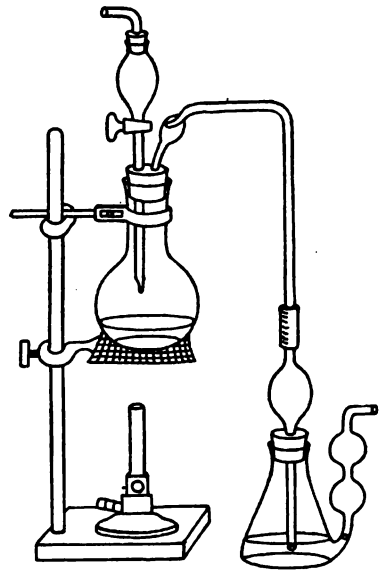

FIG. 46.

(*c*) *The sulphide is insoluble.*

(1) **Böckmann's method** (dry oxidation).—Fuse with 12 times its weight of a mixture of 6 parts of fusion mixture and 1 part of potassium chlorate. Heat gently at first, then more strongly till no more oxygen is evolved. Extract the melt with water, filter and wash; acidify filtrate and washings with hydrochloric acid and ppt. the sulphate as $BaSO_4$.

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(2) **Lunge's method** (wet oxidation).—The very finely-ground mineral is treated in a 300 c.c. covered beaker with a mixture of 3 volumes of strong nitric and one of strong hydrochloric acid, warming gently if necessary to start the action.

Any sulphur deposited is dissolved by adding a little potassium chlorate.

Boil, transfer to a basin, evaporate dry on water-bath, treat with very dilute hydrochloric acid and filter if much insoluble matter is present.

Now free the liquid from iron by first making strongly alkaline with ammonia and then raising to the boil. (Treadwell states that this avoids the formation of an insoluble basic ferric sulphate.) Filter and wash; concentrate to about 250 c.cs. (if necessary) and ppt. with barium chloride.

GROUP II.

Hypophosphorous acid.—(1) Oxidise by adding 5 c.cs. of fuming nitric acid for every 0·5 gm. of substance dissolved in 100 c.cs. of water. Evaporate to a small volume on the water-bath, repeat with a few drops of nitric acid and determine the phosphoric acid thus formed.

(2) The solution, rendered acid with hydrochloric acid to set free phosphorous acid, is treated with excess of mercuric chloride solution and left overnight in a warm place. Filter the pptd. mercurous chloride through a Gooch crucible or tared filter and dry at 110°.

$$H_3PO_2 + 4HgCl_2 + 2H_2O = 2Hg_2Cl_2 + H_3PO_4 + 4HCl.$$

Hence $$2Hg_2Cl_2 = H_3PO_2.$$

GROUP III.

Phosphorous acid.—Similarly to method (1) for hypophosphorous acid.

Sulphurous acid.—Oxidise to sulphuric acid by treatment with bromine water or ammoniacal hydrogen peroxide and determine as $BaSO_4$.

Boric acid (*Rosenbladt-Gooch method, Zeit. f. anal. Chem.*, xxvi., 18, 364).—The boric acid is distilled as methyl borate, saponified by lime and the residue of calcium borate heated. The gain in weight $= B_2O_3$.

Heat about a gram of *pure* quicklime in a crucible over the blowpipe to constant weight. Transfer it to a conical flask and put the crucible (with any lime adhering to it) in a desiccator.

Shake the lime in the flask with a little water and connect up as shown in Fig. 47.

The aqueous solution of the borate, which must not contain more than 0·2 gm. B_2O_3, is just acidified with acetic acid, litmus being added as an indicator.

This is run into the retort and the funnel washed several times with 2 c.cs. of water. Distil off the liquid into the lime flask by immersing the retort in an oil-bath at 130°. Allow the retort to cool by removing the bath, add 10 c.cs. of *pure* methyl alcohol and again distil off. Repeat six times, acidifying the contents of the retort if they become alkaline.

The contents of the receiver after thorough shaking and standing aside are transferred to a basin and evaporated dry on a water-bath *without ebullition*,

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or boric acid will be lost. Ignite gently to destroy any acetate formed. Transfer to the original crucible (dissolving the last traces off in dilute nitric acid). Evaporate dry on water-bath. Ignite gently at first, afterwards to constant weight.

Boric acid in minerals, enamels, glass, etc., is obtained by fusing with six times its weight of fusion mixture in a platinum crucible, extracting the melt with water, filtering, washing and evaporating the filtrate and washings to a small volume. Then treat as above.

Boric acid in mineral waters (soffioni, etc.) is also done in this manner after *rendering alkaline* a large volume of the water and evaporating to small volume. Remember that free boric acid is volatile with steam.

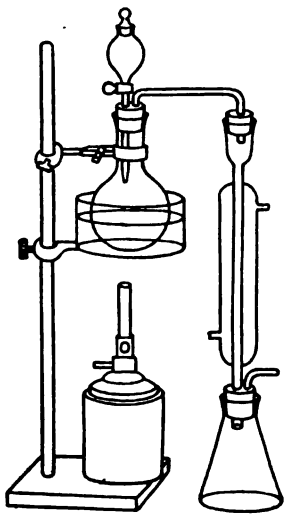

FIG. 47.

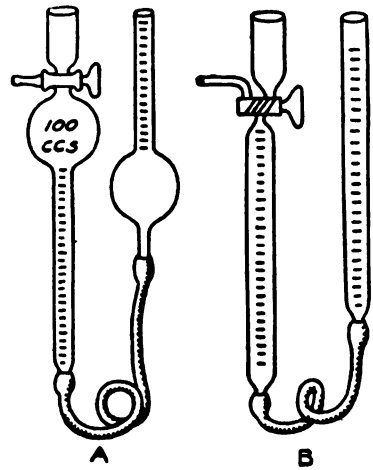

FIG. 48.

Thiosulphuric acid.—Estimated by oxidation to sulphuric acid with ammoniacal hydrogen peroxide.

Nitric acid. (1) *Lunge's method.*—Owing to the solubility of all nitrates there is no gravimetric method. The simplest and most easily performed method is by using the Lunge nitrometer (Fig. 48). The nitric acid is reduced to nitric oxide by mercury, and the volume of NO measured.

An amount of nitrate sufficient to give between 100 and 120 c.cs. of NO is weighed out, and placed in the funnel of the nitrometer. The bulb and the bore of the tap have previously been filled with mercury by raising the levelling tube and opening the tap. It is now treated with a few drops of water and drawn into the bulb by lowering the levelling tube and cautiously opening the tap. *Care must be taken not to draw any air into the bulb.* Rinse out the funnel with two lots of 0·5 c.c. of water, drawing each into the bulb as before, and then draw in two lots of 7 c.cs. each of strong sulphuric acid.

Now hold the measuring tube by the top and bottom, with the thumb on the tap to prevent it from falling out, and shake gently so as to bring the

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liquid into intimate contact with the mercury. *Do not touch the bulb with the hand.*

After 2 minutes shaking allow to stand for 5 minutes, read the volume after adjusting the mercury levels, and repeat the shaking for another minute to see if the action is complete. Leave for another 5 minutes and then adjust to atmospheric pressure as follows. Mercury has a S.G. of 13·6, or about seven times that of the sulphuric acid in the bulb. Read the *height* of the sulphuric acid column in mms., divide this by 7, and raise the mercury in the levelling tube to this height above the mercury in the measuring tube. The levelling tube is usually graduated in mms. to facilitate this.

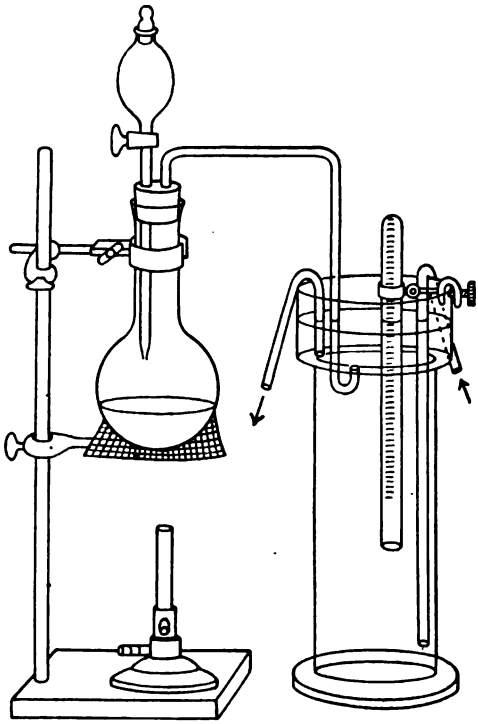

FIG. 49.

Read the volume of NO, the temperature of the room, and the barometer.

Reduce the volume to N.T.P., and calculate the weight of nitric acid produced.

From the equation

$$6Hg + 2HNO_3 + 3H_2SO_4 = 2NO + 4H_2O + 3Hg_2SO_4$$

we see that

$$NO = HNO_3$$

$$30{\cdot}01 = 63{\cdot}02,$$

and a litre of dry NO weighs 1·3419 gm. at N.T.P.

(2) *Schlösing's method, modified by Grandeau and by Wagner.*—When a

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nitrate is added to an acid solution of a ferrous salt, it is wholly reduced to nitric oxide. Air must of course be entirely excluded.

The apparatus is shown in Fig. 49.

A flask of 250 c.cs. capacity is fitted with a rubber stopper as shown. (The funnel tube should be drawn out.)

Run into the flask about 40 c.cs. of a 40 % solution of ferrous chloride (which can be made by dissolving wire nails in strong hydrochloric acid) and 40 c.cs. of strong hydrochloric acid (2 vols. pure acid : 1 vol. water). *The bore of the tap and the tube of the funnel must remain filled with this solution.* The contents of the flask are now boiled till all air is expelled, meanwhile allowing cold water to circulate through the trough. When air is all displaced (test with a test-tube filled with water) invert a measuring tube full of water over the delivery tube. A small quantity of solution of weighed amount of nitrate is placed in the funnel and run drop by drop into the boiling ferrous chloride. When *nearly* all has run in, close the tap, put 20 c.cs. of the hydrochloric acid into the funnel and run into the flask. Repeat this. No air bubbles must be allowed to get into the flask. Continue the boiling till the nitric oxide has all been carried over. Remove the measuring tube from the delivery tube and fix it in a clamp. After standing for 5 minutes lower it into the trough till the water levels inside and outside are the same and read the volume of gas. Reduce to N.T.P. (remembering that it is saturated with water vapour) and calculate as before.

Chloric acid.—Chlorates are reduced to chloride by boiling for 15 minutes with 10 % ferrous sulphate solution. The liquid is then treated with sufficient nitric acid to dissolve the basic ferric sulphate and pptd. with silver nitrate.

In presence of chloride (usually the case) the chloride chlorine is estimated in a separate sample, then the total chlorine after reduction. The difference is the chlorate chlorine.

Perchloric acid.—The salt is mixed with four times its weight of pure ammonium chloride and *gently* ignited in a platinum crucible. Determine the chlorine in the residue as silver chloride.

Silicic acid. Silicon.—The determination of silica in silicates has been described on p. 215.

Determination of silicon in iron and steel.—Not less than 5 gms. of the turnings (which have been freed from oil by washing with ether) are weighed into a beaker and treated with 50 c.cs. of a mixture of 3 vols. nitric acid, 1 vol. hydrochloric acid, ½ vol. water, and the beaker at once covered. Warm gently on the hot-plate in draught-cupboard till action starts, then remove to a cool part of the plate. When completely dissolved boil gently on the hot-plate and then transfer to a basin, rinsing the beaker and cover into the basin also. Evaporate dry on a sand-bath with gentle heat and *constant* stirring, and heat gently when quite dry to decompose the ferric nitrate and to dehydrate the silicic acid formed from the iron silicide. (Unless the stirring has been sufficiently vigorous to prevent the mass from caking, the basin will break during ignition.) The phosphide will now be in the form of phosphate, sulphide as sulphate.

Allow to cool, treat with 50 c.cs. of strong hydrochloric acid, stir thoroughly and heat to 90° for some time. Everything now dissolves except silica and

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graphite. Evaporate on the *water-bath*, moisten the residue with strong hydrochloric acid, dry again, again moisten with hydrochloric acid and set aside for half an hour. Dilute with 150 c.cs. water, boil, filter off the silicic acid, wash it and ignite it wet. Weigh as SiO_2.

Note.—If the silica is pink, it contains ferric oxide. If it is grey it contains graphite.

In the first case fuse with fusion mixture. In the second case fuse with fusion mixture and potassium nitrate. Dissolve the melt in water, acidify strongly with hydrochloric acid, evaporate on the water-bath and treat as before. (Remember, two filter ashes.)

Determination of phosphorus.—It is usual to determine the phosphorus in the same operation. The filtrate from the silica will contain it as phosphoric acid. It is evaporated dry, dissolved in the minimum of nitric acid and pptd. by Woy's method, page 197.

Hydrofluoric acid. *Penfield's method.*—The fluoride is mixed with ten times its weight of finely powdered and ignited quartz and decomposed in a flask fitted with tap-funnel and delivery tube by heating with strong sulphuric acid. The silicon tetrafluoride evolved is "scrubbed" by passing through a calcium chloride tube filled with *dry* glass-wool, and then through two U-tubes each containing 20 c.cs. of potassium chloride solution in 50% alcohol. The fluo-silicic acid produced by the contact of the fluoride with water is decomposed thus by the potassium chloride

$$2KCl + H_2SiF_6 = 2HCl + K_2SiF_6.$$

Finally aspirate air through the apparatus and titrate the contents of the U-tubes with $\frac{N}{5}$ caustic soda, using litmus or lacmoid as indicator. (See Volumetric Analysis.)

From the above equation it is seen that $2HCl = 6F$.

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PART II.

ELECTROLYTIC METHODS.

THE electrolytic determination of the metals is not only very convenient, as the experiment can be started overnight and the weighings made next morning, but has been brought to a high degree of accuracy. The difficulties

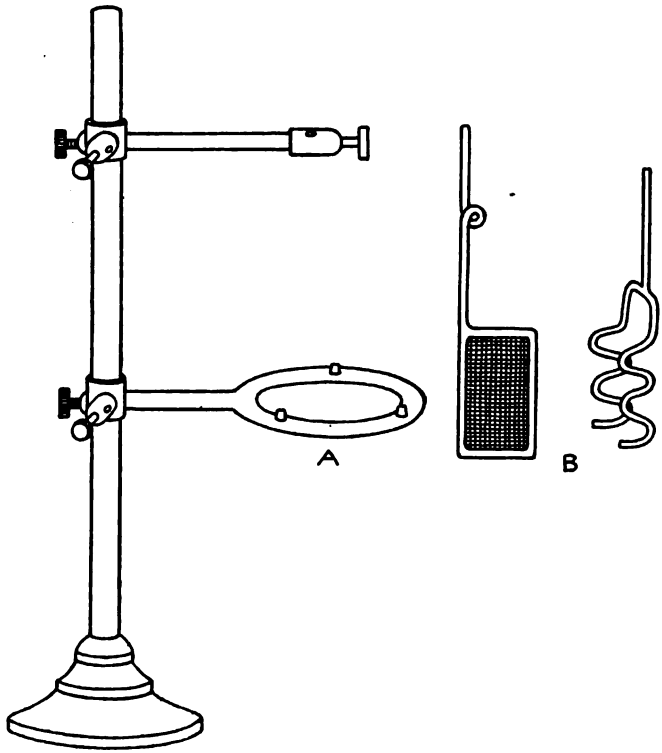

FIG. 50.

to be overcome are chiefly in the direction of finding suitable solutions, potential differences and current densities which give a firm coherent deposit of metal in a quantitative manner. Unfortunately, in many cases, conditions which give a good deposit lack accuracy, and *vice versa*.

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Nevertheless these difficulties have been overcome by the work of many experimenters, notably Classen, F. M. Perkin, and many American chemists. The convenience lies in the fact that there are no tiresome filtrations and washing of ppts.; moreover, separations can readily be effected by a suitable alteration in the E.M.F. applied, and metals can be deposited one after the other.

There are now numerous devices and refinements which very considerably shorten the time necessary for an analysis, so that the determination of a metal can be accomplished in far less time and with as high a degree of accuracy, as by the usual pptation. methods. Chief amongst these was the introduction of the rotating electrode, the electrode on which the deposit was to be made being caused to rotate during the whole experiment. This stirs the solution and considerably shortens the time necessary for the deposition.

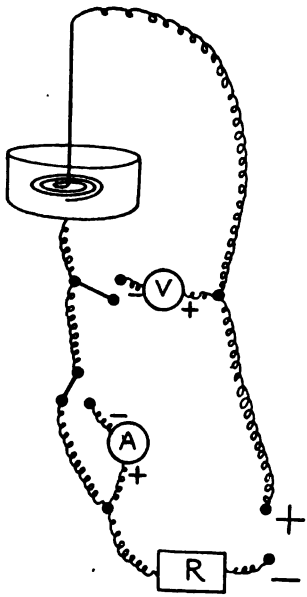

FIG. 51.

Text-books on the subject should be consulted for the full description and use of these. We shall here content ourselves with describing a few determinations that can be readily and accurately carried out with simple apparatus.

The chief necessities are a platinum basin of about 180 c.cs. capacity, as the container and cathode, and a flat spiral of thick platinum wire as anode. A special stand, fitted with terminals and platinum contacts for the basin is also required (see Fig. 50 A).

For some of the determinations described the "flag" electrode is preferable. This is a flag-shaped piece of apparatus of platinum gauze in a stout frame, also of platinum, and a wire to support it (see Fig. 50 B).

The other necessaries are: a suitable source of current (accumulator batteries charged from the town mains are best), a variable resistance, the type with some form of sliding contact being the most accurate, and a voltmeter and ammeter, each reading up to 5 units in tenths.

The connections will be readily understood from Fig. 51. It is convenient to arrange both ammeter and voltmeter with a switch so that they can be thrown in and out of circuit, and current need not therefore pass through them during the whole experiment, but only when necessary to take readings. The resistance is for the small adjustments of P.D. which may be necessary at the terminals of the electrolytic cell.

The two most important factors in determinations are current density (C.D.) and E.M.F.

Current density is defined as *ampères per sq. decimeter of cathode surface.*

In all the following experiments the volume of the solution should be made up to 120 c.cs. The surface area of the basin in contact with this volume of liquid can be calculated once for all.

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The following points are of great importance:

1. The deposit of metal on the basin must be kept covered with the solution during the whole experiment. If the cell gets hot evaporation will take place and the deposit that is thus uncovered will surely be spoiled.

2. A test is usually necessary as to when the experiment is finished. This is most easily done by withdrawing two or three drops with a pipette and testing for the substance in question by any *sensitive* qualitative test already described.

3. Breaking the circuit is frequently not permissible so long as the deposit is in contact with the electrolyte. This is especially the case when solutions containing nitric acid are being electrolysed, as the moment the current ceases to flow the acid exerts a solvent action on the deposit. In such cases as these, distilled water should be allowed to run into the basin from a large separating funnel on one side, and a small syphon on the other side carries away the electrolyte *at the same rate*. This goes on until the current almost ceases, when the circuit may be broken.

4. Washing and drying the deposit should be carried out the moment the circuit is broken. Distilled water is used, followed by absolute alcohol. (*Industrial* methylated spirit distilled from caustic soda and then again from quicklime may be used, but *not* ordinary methylated spirit, which contains paraffin.) The final drying may be done in the steam oven unless otherwise stated. (This usually takes only a few minutes.)

The conditions in the following experiments are suitable for all-night or all-day determinations.

The E.M.F. given is that between the terminals of the electrolytic cell. In no case should the E.M.F. employed, nor the C.D. differ from the figures given by more than a tenth of a unit.

Silver.—For every gram of silver salt add 4 gms. of purest potassium cyanide and 120 c.cs. of water. C.D. 0·3 amp.; E.M.F. 3·5 volts.

Wash as described and dry at 100° C.

Lead.—Lead is determined as PbO_2 on the *anode*, and must be in the form of nitrate.

Dissolve about 1 gm. in water, add 25 c.cs. of concentrated nitric acid and dilute to 120 c.cs. The basin of course is made the *anode* in this determination. C.D. 0·75 amp.; E.M.F. 2·2 volts.

Wash by syphon. Dry at 200°.

Mercury.—A "flag" electrode is best. The area may be reckoned as if it were made of metal foil instead of gauze. (Remember that both sides are used.) A convenient size usually supplied has an area of half a square decimetre.

About a gram of the salt is dissolved in water, 1-2 c.cs. of concentrated sulphuric acid added, and the volume made up to 120 c.cs. C.D. 0·6 amp.; E.M.F. 3·5 volts.

Syphon washing is unnecessary. Break the circuit when the electrolysis is complete and quickly pour out the liquid and wash with cold distilled water. Do not use alcohol, which will spoil the deposit, nor heat, which will volatilise mercury. Dry in a desiccator.

Insoluble mercury compounds and organic preparations may be electrolysed by adding potassium cyanide to the suspension in water.

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It is better in the case of organic preparations containing mercury to heat them with a very little concentrated nitric acid and then to dilute and add the cyanide. Employ about a gram of the compound and about 4 gms. of pure cyanide.

Copper.—About a gram of the salt is dissolved in water, 12 c.cs. of strong nitric acid are added, and the whole is diluted to 120 c.cs. C.D. 0·3 amp.; E.M.F. 2·5 volts.

Wash with syphon and break circuit when the acid is washed away. Wash with water and then alcohol. Dry at 100°.

Tin.—Dissolve about 1 gm. in water and add *yellow* ammonium sulphide till the ppt. first formed redissolves. Dilute to 120 c.cs. Neglect any ppt. of sulphur, which can be removed from the final deposit with a "policeman" or a camel-hair brush. C.D. 1 amp.; E.M.F. 3·5 volts.

Nickel.—The salt employed is nickel ammonium sulphate in ammoniacal solution. Nitric acid and nitrates must be absent. If present they are removed by evaporating with dilute sulphuric acid till thick white fumes come off.

Employ about 1 gm. of the salt, 5 gms. of ammonium sulphate, 35 c.cs. of ·880 ammonia, and make up to 120 c.cs. with water. C.D. 0·5 amp.; E.M.F. 3 volts.

Cobalt.—Similarly to nickel. C.D. 0·4 amp.; E.M.F. 3 volts.

SEPARATIONS.

Copper from silver (sterling silver, etc.).—Dissolve the salt in water and add nitric acid exactly as for copper. Electrolyse with C.D. 0·3 amp.; E.M.F. 1·3 volts and *no higher*.

A deft manipulator can break the circuit, pour out the liquid and wash quickly before the silver deposit is affected. Otherwise the solution must be evaporated to a suitable volume. *Remember to add the washings to the rest of the electrolyte.*

After weighing the silver the copper may be deposited by increasing the voltage to 2·5.

Copper from nickel (coinage, etc.).—The nitric acid solution prepared as described under copper is employed. The copper is first deposited exactly as already described. The remaining solution is evaporated with dilute sulphuric acid till thick white fumes come off and then treated exactly as under nickel.

We shall content ourselves with the above determinations which will suffice to give the student a working knowledge of the principles and manipulation of electrolytic analyses. For further information see literature.

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PART III.

VOLUMETRIC METHODS.

CHAPTER I.

INTRODUCTORY.

The principle of volumetric analysis is to cause the substance to be estimated to undergo a definite quantitative reaction with a solution of a reagent of which the strength is accurately known. From the volume of this reagent used *exactly* to complete the reaction, the quantity of substance to be found can be readily calculated by means of the equation.

The *exact* completion of the reaction is recognised by means of **indicators**, which may be:

(1) Substances which change colour with the slightest excess of reagent (*e.g.* litmus, etc., for acids and alkalis).

(2) Substances which give coloured products with the substance being determined or with excess of the reagent (*e.g.* potassium chromate and iron alum in silver titrations, *q.v.*).

(3) The formation of a ppt. (*e.g.* use of barium chloride, etc.).

(4) The colour of the reagent itself (*e.g.* permanganate).

The necessary measuring instruments are

(1) The graduated flask.
(2) The pipette.
(3) The burette.

The first named is usually graduated to *contain* the volume marked on it, the two last to *deliver* it.

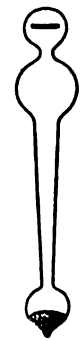

FIG. 52.

The most convenient form of burette is Mohr's, to hold 50 c.cs., graduated in tenths of a c.c. It has a glass tap, obtainable in various forms, and may also be furnished with a milk-glass back down which runs a blue line, to facilitate reading. A burette float, however, will generally be found more useful and far less expensive (Fig. 52).

It is assumed that the student is already familiar with the appearance and use of these instruments, as they are described in most elementary school chemistry books, as also is the obvious method of reading them to avoid error due to parallax.

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The pipette, it may be remarked, is used as follows:

Dip the point *well below the surface* of the liquid, as, if air bubbles get in, the liquid is inevitably drawn into the mouth. Suck the liquid to a point above the graduation, close the top with a *slightly damp* (not wet) forefinger, and *lift the point out of the liquid.* Now by slightly releasing the pressure, with the graduation held level with the eye, the liquid is allowed to run out at any desired rate. The graduation should be exactly tangential to the extreme lower curve of the meniscus.

To empty the pipette, *one* method should always be employed. This may be *one* of the following (adopt one method and use it *invariably*):

(1) Allow to drain for a few seconds and blow out the last drop (once only).

(2) Allow to drain for a few seconds and touch the point against the side of the vessel.

(3) Allow to drain for a few seconds and touch the point on the surface of the liquid.

It should be unnecessary to remark that a vessel which is being used to *deliver* a known volume of a solution of definite strength should always be rinsed out with a little of the solution before being filled with it. This is *not*, of course, the case when the vessel is going to *contain* a known volume of the solution, which is measured *into* it, *except* in the case where, say, a litre of a definite solution is required and the litre flask is wet with water. Students frequently get very confused on this point. A little thought should make it quite clear.

Calibration of measuring vessels.—It is important that all vessels used should bear *exact* relationship to one another. It does not matter if the vessels are graduated in true c.cs. or in other varieties of c.cs., provided that, say, the 50 c.c. pipette, twice emptied into the 100 c.c. flask, exactly fills it; that the 50 c.c. burette delivers as much as the 50 c.c. pipette, and so on.

It will usually be found on testing the ordinary type of instrument supplied to laboratories, that this is far from being the case. By far the best plan is to purchase pipettes and flasks ungraduated and to mark them oneself.

A flask is graduated thus:

First it is cleaned with caustic soda solution, water, chromic acid solution, water, distilled water (in the order named) and thoroughly dried by gently warming and drawing a current of air through.

It is now exactly counterpoised on a suitable balance, by means of sand or shot; the required number of grams are placed on the right-hand pan, and distilled water at a definite temperature added to the flask till exactly counterpoised. (No drops must adhere to the neck; remove any with a roll of filter-paper: add or subtract minute quantities of water by means of a capillary used as a pipette.)

N.B.—Use water at the same temperature for all subsequent calibrations. In this country about 15° *C. will be the average laboratory temperature.*

Now mark the exact level of the lower part of the meniscus with a *straight* strip of gummed paper. Cover paper and glass with the thinnest possible coating of paraffin or bees-wax, and cut a circle in the wax with a sharp knife, level with the edge of the paper. This is best done by standing the flask on the bench, supporting the knife firmly at the necessary level by a clamp,

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pressing the flask against it and turning the flask round. Paint the mark with hydrofluoric acid, and after three minutes wash well and remove the wax.

Similarly etch the volume on the bulb of the flask.

Pipettes have to be calibrated by trial. Gum a thin strip of paper longitudinally along the stem approximately where the graduation will come. (First cleanse the pipette as described above; it may be left *wet with distilled water at the required temperature.* Close the point with the thumb and fill it with distilled water from another pipette of the required volume. Make a faint straight pencil mark on the paper at the level of the meniscus curve, and allow the water to run into a tared beaker and weigh. If incorrect, fill the pipette again by suction to an estimated mark, and so on by trial till the required volume is arrived at. Then etch the mark as before.

A burette may be calibrated in one of two ways.

(1) By running out, say, 5 c.cs. (on the scale) at a time, weighing the water so delivered, and plotting a curve of scale-readings–volumes.

(2) By running out a succession of exactly equal volumes, and noting the corresponding scale-readings. A volume–scale-reading curve is drawn.

The manner of carrying out the first method will be self-evident.

The second method is carried out as recommended by Ostwald. It has the advantage of necessitating only one weighing. A small pipette, shaped as shown in Fig. 53 is attached to the burette. The rubber tube *t* contains a short piece of glass rod, and the liquid can be run out of the pipette by compressing this to the shape shown in the section in the sketch.

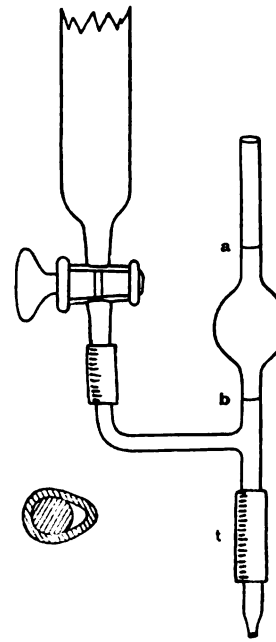

FIG. 53.

The pipette has two marks at *a* and *b*, the exact capacity being immaterial, but about 5 c.cs.

The burette and pipette having been cleaned as already described, and filled with distilled water at the desired temperature, the pipette is just filled to mark *a*. By pinching *t* the water is run out to mark *b* into a tared beaker and weighed. By carefully opening the burette tap the pipette is again filled to mark *a* and the corresponding burette reading taken. Repeat as necessary. The weighing gives the volume of the pipette, which is of course constant. Thus we get a series of figures showing the relation between scale-readings and actual volumes. A curve is plotted and used with the burette.

Note.—In connection with the calibration of vessels, it should be noted that there are three different "litres" in common use:

(1) The true litre, which is the volume of a kilogram of water at 4° C., weighed in a vacuum.

(2) The Mohr litre, which is the volume of a kilogram of water at 17·5° C. in air.

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(3) The "normal" litre, which is the volume of a kilogram of water at 15° C. in air.

As already pointed out, it is immaterial which, if any, of these is taken by the student in calibrating his vessels. All that is required is that they should agree amongst themselves. The last-named "litre" is probably the most convenient, as it most nearly approximates to the average room temperature in this country. The only necessity is that all should be calibrated with water *at the same temperature.*

It may be remarked that it is extremely easy to calibrate accurately to within ·01 % error by the above methods.

Strengths of reagent solutions.—These are usually expressed in terms of Normal. Normal strength is such that a litre of solution contains 1 gram *equivalent* of the *active part* of the reagent.

In the case of	acids	this is	acidic hydrogen.
,, ,,	alkalis	,,	hydroxyl.
,, ,,	salts	,,	the metal or the acid radical.
,, ,,	oxidising agents	,,	*available* oxygen.

Etc., etc.

Note that it is of importance to know in what light we are to regard the reagent before we can state what a normal solution is.

E.g., a normal solution of $KMnO_4$, regarded as a *salt*, would contain 1 gm.-molecule per litre; regarded as an oxidising agent, 0·2 gm.-molecule per litre, since $2KMnO_4 \rightarrow 5O$ (available).

To get the most accurate results, the strength of the solution of the reagent should approximate to the strength of the solution of the substance being estimated.

The strength of the solution of a reagent is often called its *titer*.

The act of running a reagent from a burette into a solution to be estimated is called *titrating* the latter with the former.

The volume of a reagent used in one titration should not as a rule be much less than 10 c.cs. or the relative error in reading, etc., will be out of proportion to the accuracy otherwise attainable.

N.B.—Before taking any standard solution out of the stock-bottle, shake well, as water always distils from the solution on to the shoulders of the bottle. Needless to say, the stopper of the bottle must fit accurately, and drops of reagent which may accidentally evaporate and crystallise on the lip of the bottle must be removed.

Taps of burettes should always be cleaned and dried after use, and the slightest possible smear of vaseline put on them. Otherwise they will inevitably seize. This is especially necessary after the burette has been used for alkalis.

"Water" throughout the following pages always means distilled water unless otherwise definitely stated.

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CHAPTER II.

ACIDS AND ALKALIS.

THE strength of acids is found by titrating with alkali of known strength, and *vice-versa*.

Indicators.—Those in most common use are:

Litmus.—Red with acids, blue with alkalis.

Phenolphthalein.—Colourless with acids, purple with alkalis.

Methyl-orange.—Pink with acids, yellow with alkalis.

A mixture of the two last-named may be used as a neutral indicator. It is pink when acid, yellow when neutral, purple when alkaline.

Litmus solution is made by grinding the best commercial product with water, pouring into a gas-jar to settle and syphoning off the clear liquid. It will usually be slightly alkaline, and should be tested. One drop of $\frac{N}{10}$ acid should suffice to turn red at least 5 c.cs. of the solution. If this is not the case very dilute hydrochloric acid should be added to the bottle, a drop at a time, till the purple neutral colour is reached. The stock-bottle should be left open to the air or decomposition will set in.

Phenolphthalein solution is made by dissolving about 1 gram in 100 c.cs. of 50 % alcohol.

Methyl orange solution is made by treating 0·5 gm. with 100 c.cs. of boiling water and filtering when cold.

Methyl orange is the least sensitive of the above indicators. One drop is usually sufficient.

Indicators are conveniently kept in dropping bottles.

The characteristics of the above indicators are as follows:

Litmus is more or less affected by weak acids like carbonic, boric, etc.

Phenolphthalein is affected more easily by carbonic, boric, etc. acids.

Methyl orange is not affected by these acids, and is only slowly affected by organic acids.

Hence:

Litmus (cold) is suitable for titrating mineral acids and oxalic acid with alkaline and alkali earth hydroxides.

If the solution is boiling it can also be used for the carbonates and sulphides of sodium and potassium.

Phenolphthalein (cold) for all acids except very weak ones as carbonic, boric, etc., with alkali and alkali earth hydroxides, *except ammonia*. Boiling, it can also be used for carbonates, *except ammonia*.

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Methyl orange, being unaffected by very weak acids, can be used for titrating the hydroxides, carbonates, sulphides, silicates and borates of the alkalis and alkali earths (where soluble) with *mineral* acids. It should *not* be used with organic acids.

Preparation of normal acids and alkalis.—In only a few cases is it possible to obtain alkalis and acids in a sufficient state of purity to weigh out the required quantity and dissolve in the required amounts of water.

These cases are :

Alkalis.—Sodium carbonate (pure anhydrous only).
Borax.

Acids.—Oxalic only.

To make normal sodium carbonate.—Take about 60 gms. of the purest anhydrous salt obtainable, gently heat in a platinum or silver basin for 20 minutes to be sure it is completely dehydrated, and weigh out exactly 53 gms. on a tared clock-glass. Place a funnel in a litre flask, tip the substance into the funnel and rinse it into the flask with *hot* water. Thoroughly rinse the clock-glass and funnel into the flask, allow the solution to cool and carefully make up to 1000 c.cs. with constant shaking. Finally shake thoroughly.

Since 1 c.c. of this solution contains ·053 gm. of Na_2CO_3, the strength of any acid solution can be readily found by measuring, say, 10 c.cs. of the acid into a flask, adding a drop of methyl orange and running in N. Na_2CO_3 solution till the last drop added changes the colour of the indicator from pink to yellow. Then from the equations it will be seen that 1 c.c. of the soda solution will neutralise :

·03647 gm. HCl,
·04905 gm. H_2SO_4,
·0630 gm. HNO_3, and so on.

The calculation of the weight of acid in the volume taken for analysis is sufficiently obvious.

Solutions of soda stronger than N. are seldom if ever required. Solutions any desired fraction of N. strength are made by measuring a known volume of N. solution and diluting to the required volume.

Decinormal borax solution.—Owing to methyl orange being quite unaffected by free boric acid, a solution of borax behaves, on titration with acid in presence of methyl orange, just like an alkali carbonate or hydroxide.

On account of the ease with which borax can be obtained pure, and also of its high equivalent weight, it is a very suitable substance to use for making $\frac{N}{10}$ (decinormal) alkali.

$$Na_2B_4O_7, 10H_2O = 382{\cdot}1. \quad \text{Equivalent} = 191{\cdot}05.$$

Hence 19·105 gms. of borax will be required to make a litre of decinormal solution.

The solution is made as already described for sodium carbonate.

1 c.c. of this solution, with *methyl orange* as indicator, will react with :

·003647 gm. HCl,
·004905 gm. H_2SO_4, and so on.

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Note.—It is not advisable to attempt to make a borax solution stronger than $\frac{N}{5}$ owing to the limited solubility of borax at low temperatures.

To make normal oxalic acid.

$$H_2C_2O_4, 2H_2O = 126{\cdot}05. \quad \text{Equivalent weight} = 63{\cdot}03.$$

Hence weigh out exactly 63·03 gms. of the purest recrystallised oxalic acid obtainable, and dissolve and make up to a litre of solution as already described. The solution does not keep very well, and should only be employed when a N. acid solution is wanted at once (as in an examination).

The best indicator to use is litmus in boiling solution.

To make normal sulphuric acid.

$$H_2SO_4 = 98{\cdot}1. \quad \text{Equivalent weight} = 49{\cdot}05.$$

As we cannot weigh out 49·05 gms. of pure H_2SO_4 and dilute to a litre, the method employed is to make a solution slightly stronger than normal, titrate with normal alkali and calculate how much water to add to make it exactly normal. For this purpose a Giles flask is useful (though not indispensable). (See Fig. 54.)

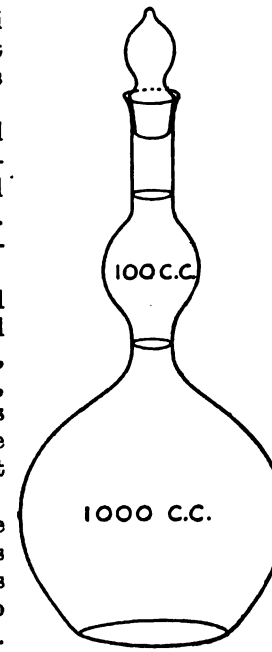

FIG. 54.

Put about 500 c.cs. of water into the flask, and slowly pour in, with shaking, 35 c.cs. of pure concentrated sulphuric acid. Allow to cool, and add water to the 1100 c.cs. mark with thorough shaking.

Rinse out a burette with the N. sodium carbonate solution, and fill it up with this solution.

Rinse out a 25 c.c. pipette with the acid, and transfer 25 c.cs. to a 120 c.c. conical flask (preferred for titrations). Add 1 drop of methyl orange, stand the flask on a white tile and run in the soda, with constant shaking, till the last drop just turns the indicator yellow. Repeat twice more. Take the mean of the three titrations, which ought not to differ by more than 0·1 c.c. at the *most*.

If the sulphuric acid is normal, 25 c.cs. of the alkali will be required for each titration. As it is stronger than normal, rather more alkali than this will be required. Calculate how much water to add to a litre of the acid to make it exactly normal. Withdraw acid from the Giles flask by means of a pipette till exactly 1000 c.cs. are left, add the calculated amount of water, shake thoroughly and bottle. (The bottle should be rinsed out with a little of the acid before filling it, for obvious reasons.)

The above calculation is best illustrated by an example.

Suppose that 25 c.cs. of the acid required 27 c.cs. of N. alkali. It is obvious that to make the acid normal, 25 c.cs. must be diluted to 27 c.cs. with 2 c.cs. of water. Hence a litre of acid will require 80 c.cs. of water. Run in from

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a burette this amount to the 1000 c.cs. of acid in the Giles flask and shake thoroughly.

In an exactly similar manner normal hydrochloric and nitric acids may be made.

Suitable quantities for the 1100 c.cs. flask are 100 c.cs. of concentrated hydrochloric and 110 c.cs. of concentrated nitric acid.

Normal sodium hydroxide.

$$NaOH = 40{\cdot}01. \quad \text{Equivalent weight} = 40{\cdot}01.$$

About 52 gms. of the best white sticks of NaOH are quickly washed with a little water to dissolve carbonate from the surface, and dissolved in water in the Giles flask (care when placing sticks in flask; do not *drop* them in !). Make up to 1100 c.cs., thoroughly shake, titrate 25 c.cs. with N. acid (hydrochloric or sulphuric) and make exactly normal just as already described for sulphuric acid. Methyl orange is the most convenient indicator. If litmus is used the solution must be boiled and the boiling continued after each addition of acid till the blue colour does not return and the change to red is permanent. This is because small amounts of carbonate are always present, and the free carbonic acid forms $NaHCO_3$ with the remaining Na_2CO_3, which turns litmus reddish slightly before the neutralisation is completed. On boiling, this is decomposed,

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2,$$

and the litmus thus turned blue again.

The same remarks apply to phenolphthalein.

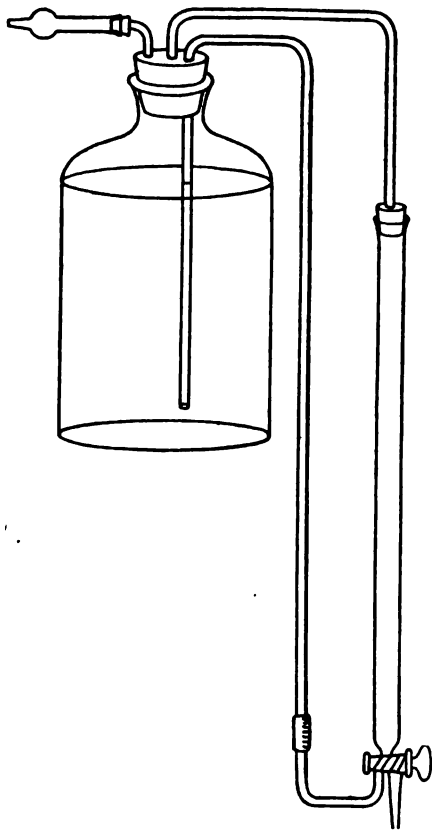

FIG. 55.

If alkali hydroxide quite free from carbonate is required, the preparation of pure NaOH is very troublesome, and when made must be very carefully preserved from the atmosphere. It is better to use baryta, $Ba(OH)_2, 8H_2O$, as $BaCO_3$ is insoluble.

To make $\frac{N}{10}$ baryta.

$$Ba(OH)_2 + 8H_2O = 315{\cdot}51. \quad \text{Equivalent weight} = 157{\cdot}8.$$

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As in the case of NaOH, we make an approximately $\frac{N}{10}$ solution and find its exact strength with $\frac{N}{10}$ hydrochloric acid, using phenolphthalein as indicator. It is not advisable to dilute to exactly normal strength, as traces of CO_2 will be introduced in the process and the strength will therefore be altered. It is therefore preserved as described below and the exact strength marked on the label.

Weigh out about 40 gms. of the crystals and dissolve in 2 litres of water. Place in the bottle shown in Fig. 55. This arrangement allows the burette to be filled and emptied without exposing the solution to atmospheric carbon dioxide. A soda-lime tube purifies air entering the bottle. Always empty the burette *after* use, and rinse out with the solution *before* use.

Titrate $\frac{N}{10}$ hydrochloric acid with the baryta solution, using phenolphthalein.

Calculate the strength in terms of normal and label it on the bottle.

Thus if 25 c.cs. of $\frac{N}{10}$ HCl require 24 of the baryta, the latter is obviously

$$\frac{25}{24} \times \frac{N}{10} = \cdot 1042 \text{ N.}$$

It may here be remarked that whilst for ordinary use it saves calculation to make all solutions *exactly* normal or a definite fraction of normal in strength, yet for examination purposes this is not usually done, but the weight of reagent per litre of solution is supplied. The simplest way to use this is to calculate the titre in terms of normal strength. Any volume of the reagent used, multiplied by this factor, gives the corresponding volume of normal reagent. Thus, sulphuric acid containing 5 gms. of H_2SO_4 per litre of solution is

$$\frac{5}{49 \cdot 05} \text{ N} = \cdot 1019 \text{ N.}$$

ALKALIMETRY

In any determination involving weighing out the substance, it is usual to weigh out sufficient of the substance for at least three titrations, to make this up to a definite volume and to withdraw a suitable fraction for each operation. This fraction is usually referred to as an *aliquot part* of the solution. (This is most conveniently a tenth.)

1. **Determination of NaOH in caustic soda.**—Weigh about 10 gms. of caustic soda in a corked test-tube. Transfer to a 250 c.c. graduated flask and add water. Weigh the empty test-tube. When the soda has dissolved, make up to 250 c.cs. with water, shake thoroughly, and wash out a 25 c.c. pipette with some of the solution. Then place 25 c.cs. in a flask, add a drop of methyl orange and titrate with N. acid. Repeat twice.

$$1 \text{ c.c. N. acid} = \cdot 04001 \text{ gm. NaOH.}$$

Hence calculate the weight of NaOH in the whole 250 c.cs. of solution, which

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will be the weight in the amount of substance weighed out. The percentage follows at once.

Note.—In this manner sodium carbonate will be calculated as NaOH. (So will traces of lime, sodium silicate, aluminate, etc.)

For separation, see next experiment.

2. **Determination of alkali carbonate in presence of alkali hydroxide.**

First Method.—Weigh out a suitable quantity as in previous experiment.

(*a*) Titrate the total alkali in an aliquot part, using methyl orange as indicator and normal acid as reagent. Take the mean of three titrations.

(*b*) To a fresh aliquot part add barium chloride till no more ppt. of barium carbonate forms. Titrate the remaining hydroxide, using phenolphthalein (cold). (Three titrations.)

The difference between the volumes of acid used in *a* and *b* will be the volume corresponding to the carbonate.

Second Method (Volhard's).—If acid be added to a sufficiently dilute solution of a carbonate, bicarbonate is formed until all the carbonate is transformed to bicarbonate. Hence:

Titrate the alkaline solution (which should not be stronger than $\frac{N}{10}$) with $\frac{N}{10}$ acid, using phenolphthalein.

When the pink colour has just disappeared

(1) All hydroxide has formed the salt.

(2) All carbonate has turned to bicarbonate.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl. \quad \text{.....(1)}$$

Now add a drop of methyl orange and continue adding acid till the indicator turns pink. Repeat twice more and take the mean.

The reaction which has now taken place is

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2. \quad \text{.....(2)}$$

A consideration of equations (1) and (2) shows at once that twice the volume of acid used for (2) is the volume of acid required to completely neutralise the carbonate. This, subtracted from the whole volume of acid added, gives the volume used for the hydroxide.

By a slight variation this method may be used to determine carbonate in the presence of bicarbonate, thus:

3. **Determination of the formula of sodium sesquicarbonate. Na_2CO_3, $NaHCO_3$, $2H_2O$.**—Weigh out about 0·75 gm. of the salt, transfer to a 100 c.c. flask, dissolve in water, make up to 100 c.cs. and shake thoroughly.

Titrate 25 c.cs. at a time with $\frac{N}{10}$ acid and phenolphthalein. Then add methyl orange and complete the titration.

The first reaction is:

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl,$$

and then

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

If the volume of acid used to render the phenolphthalein colourless be doubled, we obtain the volume of acid corresponding to the carbonate. This

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volume subtracted from the whole volume of acid added gives us the volume required for the bicarbonate.

A simple calculation thus gives us the weights of carbonate, bicarbonate and (by difference) water of crystallisation in the weight of salt taken. Hence the formula can be calculated.

N.B.—If in Volhard's method CO_2 is seen to escape before the phenolphthalein turns colourless, the solution is too strong. A fresh portion must be taken and suitably diluted.

4. **Determination of insoluble carbonates.**—Carbonates such as that of calcium may be determined by weighing out a suitable amount, dissolving in about double the necessary amount of N. acid, making up to a known volume and titrating the excess of acid in an aliquot part by means of $\frac{N}{2}$ alkali, using methyl orange.

From the amount of acid used by the carbonate, its weight can readily be calculated.

5. **Determination of ammonium.** *Method* 1.—No other base is present except sodium or potassium, and the salts are present as normal salts of mineral acids, except carbonate and other very weak acids.

Weigh out sufficient of the salt to make an approximately normal solution. Make up to a known volume and transfer three separate aliquot parts to three flasks. To each add a known excess (about double the necessary amount of N. NaOH). Boil gently (with a small funnel in the mouth of each flask to avoid loss of spray) till the escaping steam no longer contains ammonia. (Litmus-paper test.) Titrate the excess of alkali with $\frac{N}{2}$ acid.

1 c.c. N. NaOH = ·01703 gm. NH_3.

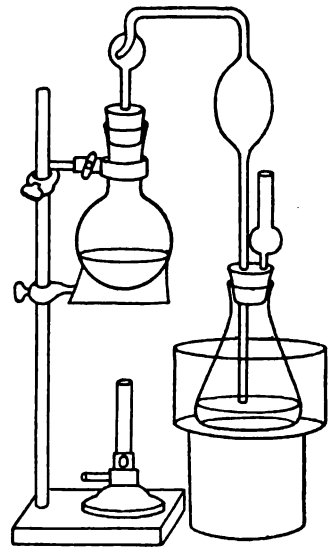

FIG. 56.

Method 2.—Other bases, or weak mineral or organic acids are present.

In this case the ammonia is driven off by boiling with NaOH and absorbed in a known excess of acid, the excess of acid being titrated with alkali. The apparatus used is that of Kjeldahl, as shown in Fig. 56.

About 1·25 gms. of ammonium chloride (or a corresponding amount of other ammonium salt) is placed in the flask and 75 c.cs. of approximately 2N. NaOH added, and the flask at once attached to the apparatus, 50 c.cs. of N. acid having been previously run into the absorption flask *through the exit tube*, which contains broken glass (best broken test-tubes). This serves to absorb traces of ammonia which may escape the main volume of acid.

Now distil rather more than half the contents of the flask into the absorption flask. Disconnect, rinse the contents of the exit tube into the absorption

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flask, make the contents up to 100 c.cs. and titrate 25 c.cs. at a time with $\frac{N}{2}$ NaOH, using litmus or methyl orange (*not* phenolphthalein) as indicator.

$$1 \text{ c.c. N. acid} = \cdot 01703 \text{ gm. } NH_3.$$

Note.—The ammonia in gas liquors, etc., is determined by this method. It is usual to take 10 c.cs. of the liquor, and to have the acid of such a strength that 10 c.c. = 1 % of NH_3 in the liquor (*i.e.* 1 c.c. = ·01 gm. NH_3), the alkali being of corresponding strength. Thus the number of c.cs. of acid used, divided by 10, give the percentage of NH_3 in the liquor without further calculation.

6. **Determination of alkali earth salts.**—The carbonates have already been dealt with.

Other salts are determined by pptg. the carbonate with a known excess of N. Na_2CO_3, filtering and washing, making up the filtrate and washings to a known volume and titrating the excess of N. Na_2CO_3 in an aliquot part.

Nothing else that reacts with Na_2CO_3 may be present.

7. **Determination of other metallic salts.**—Almost any metal may be determined similarly to the method of No. 6, using either Na_2CO_3 or NaOH, provided that:

(*a*) Nothing else is present which acts on the reagent.

(*b*) The metallic hydroxide or carbonate does not adsorb the alkali. Those which do this have already been indicated in Part I. of this book.

8. **Determination of the hardness of water** (*Hehner's method*).

Note.—The water must not contain alkali carbonates.

(i) *Temporary hardness.*—70 c.cs. of the water are titrated with $\frac{N}{10}$ HCl, with methyl orange as indicator. The titration is finished at the first sign of change (compare with a standard).

$$1 \text{ c.c. } \frac{N}{10} \text{ HCl} = \cdot 005 \text{ gm. of } CaCO_3.$$

Hence 1 c.c. of $\frac{N}{10}$ HCl = 5 degrees of hardness on Clarke's scale (grains per gallon, *i.e.* parts per 70,000) if 70 c.cs. of water were taken.

To express the hardness in French degrees (parts per 100,000) use 100 c.cs. of the water.

(ii) *Permanent hardness.*—Another 70 (or 100) c.cs. of the water is treated with excess of $\frac{N}{10}$ Na_2CO_3 and evaporated dry on the water-bath. Add some freshly-boiled distilled water to the residue, stir well, filter and wash the residue on the filter *at least* four times with boiling water. The combined filtrate and washings are diluted to 70 (or 100) c.cs. with distilled water and titrated with $\frac{N}{10}$ HCl and methyl orange.

Each c.c. of $\frac{N}{10}$ Na_2CO_3 used = 5 degrees of permanent hardness.

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ACIDIMETRY.

1. **To determine the strength of strong (fuming) acids.**—These must be weighed out, as measuring them would involve alteration of strength by fuming, absorption of moisture, etc. The Lunge and Rey pipette is used for this (see Fig. 57). To use, remove the tube, place a few drops of water in it, and weigh the two portions. Now introduce acid into the bulb by sucking out some of the air with the lower tap closed and the upper one open. Close the upper tap, dip the point of the pipette into the acid and open the lower tap. The bulb should be not much more than half-full. Close the tap, connect the pipette to the tube and weigh again. Now run the acid into some distilled water, rinsing out pipette and tube, and finally make up to 100 c.cs.

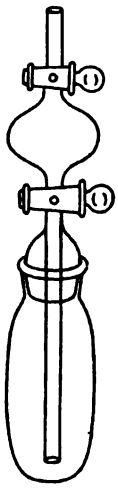

FIG. 57.

Titrate an aliquot part with N. NaOH and methyl orange.

Note.—**Phosphoric acid** may be titrated with caustic soda, using methyl orange. The indicator changes when NaH_2PO_4 is formed.

Sulphurous acid may be titrated, using methyl orange, towards which $NaHSO_3$ reacts neutral.

Hydrofluoric acid may be titrated with phenolphthalein.

Fluosilicic acid is best titrated with $Ba(OH)_2$ in alcoholic solution, using phenolphthalein.

For **organic acids** use baryta and phenolphthalein or litmus.

For **free carbonic acid** add excess of baryta and titrate the excess, using phenolphthalein.

2. **Determination of nitric acid as ammonia.**—By reduction in alkaline solution (best with Devarda's alloy, Cu 50 %, Al 45 %, Zn 5 %) nitric acid is quantitatively reduced to ammonia. This is distilled off into excess of N. acid as on p. 237.

Into the absorption flask of Fig. 24 run 25 c.cs. of $\frac{N}{2}$ acid (through the exit tube). About 0·5 gm. of the nitrate is weighed into the distillation flask, 50 c.cs. of 4N. NaOH added, and 2-3 gms. of Devarda's alloy. (Aluminium turnings may be used if the alloy is not available.)

Immediately connect up, warm gently till the reaction begins, and allow it to proceed without further heating. Then distil rather more than half the liquid into the absorption flask, and titrate the excess of acid as previously described.

Since $HNO_3 \longrightarrow NH_3$; $\therefore$ 1 c.c. of $\frac{N}{2}$ acid $= \begin{cases} \cdot 0315 \text{ gm. } HNO_3 \\ \cdot 03102 \text{ gm. } NO_3. \end{cases}$

3. **Determination of copper (indirect method),**

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

The liberated acid is titrated.

Weigh out about 2 gms. of copper sulphate or chloride crystals. Dissolve in about 50 c.cs. of water. Saturate with H_2S as described on p. 194. Filter, wash ppt. till free from acid, make up filtrate and washings to a definite

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volume and titrate an aliquot part with $\frac{N}{2}$ alkali, using methyl orange.

From the equation it follows that

$$1 \text{ c.c. } \frac{N}{2} \text{ alkali} = \cdot 01589 \text{ gm. Cu.}$$

Note.—This method is extremely accurate. It may be used for copper sulphate and chloride in the absence of bases of Groups II. and III., oxidising agents and free acids (unless the last named are separately determined).

4. **Determination of carbon dioxide in air (Pettenkofer's method).**—A stoppered bottle of about 5 litres capacity (accurately measured) is filled with the air to be tested by means of the bellows. 100 c.cs. of $\frac{N}{20}$ baryta or of saturated lime-water of accurately known titre are added, the bottle stoppered and thoroughly shaken for 15 minutes. The contents are then quickly poured into a stoppered bottle and 25 c.cs. are withdrawn and titrated with hydrochloric or oxalic acid of accurately known strength, using phenolphthalein as indicator.

It is convenient to make the acid of such a strength that 1 c.c. = 1 c.c. of CO_2 at N.T.P. (*i.e.* will neutralise as much baryta as 1 c.c. of CO_2 at N.T.P.). This is accomplished by diluting 893·2 c.cs. of $\frac{N}{10}$ acid to 1 litre. For the most accurate results water free from CO_2 is necessary both for making and diluting the acid. (See Book VI., Fig. 26.)

Remember that the volume of air used is $V - 100$ c.cs., V being the volume of the bottle. Reduce this to N.T.P. The rest of the calculation is sufficiently obvious. Express result as per cent. by volume.

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CHAPTER III.

PRECIPITATION METHODS.

A. Use of Standard Silver Solution.

THE halogens (except fluorine) may be estimated in *neutral* solution as soluble halides. Potassium chromate or arsenate is used as indicator, giving a red ppt. with the least excess of silver solution. This ppt., however, cannot form so long as any soluble halide is present, nor will it form in acid solution, in which it is soluble.

1. **Preparation of $\frac{N}{10}$ silver nitrate.**

$$AgNO_3 = 169{\cdot}89. \quad \text{Equivalent weight} = 169{\cdot}89.$$

Weigh out 16·989 gm. of purest silver nitrate, previously dried at 100° C. Dissolve in water and make up to a litre.

$$1 \text{ c.c. } \frac{N}{10} AgNO_3 = {\cdot}003546 \text{ gm. chlorine.}$$
$$= {\cdot}007992 \text{ gm. bromine.}$$
$$= {\cdot}012692 \text{ gm. iodine.}$$

2. **Standardisation of silver nitrate.**—Pure sodium chloride (see p. 52) is gently heated in a platinum basin, cooled in a desiccator and exactly 5·846 gms. weighed out, dissolved in water and made up to a litre.

The titration is performed thus: The silver nitrate must *always* be in the burette, or the indicator will not work. 10 c.cs. of the $\frac{N}{10}$ sodium chloride are placed in a flask, 1 c.c. of 5 % potassium chromate (not dichromate) is added, and the silver solution is run in till the last drop gives a permanent red tinge to the liquid. Exactly 10 c.cs. of the silver solution should be required.

3. **The determination of chlorides and bromides** is carried out similarly.

4. **The strength of a silver solution** may also be thus determined. It must be *neutral* and must be put into the burette, and $\frac{N}{10}$ sodium chloride titrated with it.

Sodium arsenate may be used as indicator if preferred. It has the advantage of being colourless.

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5. **Determination of iodides.**—The above method is unsuitable, owing to the powerful adsorptive properties of silver iodide both for silver nitrate and alkali iodide. (See under ammonium thiocyanate.)

6. **Determination of barium chloride.**—Owing to the pptn. of the indicator as $BaCrO_4$ it is necessary first to ppt. the barium with a slight excess of sodium sulphate (free from chloride) before adding the indicator. Then proceed as before.

7. **Determination of other bases.**—Any substance which is present in such a form that it can be quantitatively changed to the chloride by evaporation with strong hydrochloric acid and subsequent heating to 120° can be readily and accurately estimated by silver nitrate as above.

8. **Determination of hydrochloric acid.**—It is first titrated with sodium carbonate (any strength). The exact amount of sodium carbonate necessary to neutralise it is then added to a measured volume and the solution titrated with silver nitrate as above.

9. **Determination of chloride in presence of hydrochloric acid.**—The free acid is first determined by titrating with $\frac{N}{10}$ sodium carbonate.

Another portion, exactly neutralised by addition of the required quantity of carbonate is then titrated with $\frac{N}{10}$ silver nitrate. This gives the total chlorine. The chlorine already found as HCl, deducted from this total, gives the chlorine as chloride.

The procedure for the determination of chlorides in presence of other acids is similar. *E.g.*

10. **Analysis of a mixture of hydrochloric and sulphuric acids.**—Titrate the total acidity with $\frac{N}{10}$ sodium carbonate. Exactly neutralise a further portion with the required quantity of carbonate and titrate the chloride with $\frac{N}{10}$ $AgNO_3$. This chlorine, calculated as HCl and deducted from the total acidity gives the sulphuric acid.

11. **Determination of chlorides in tap water, etc.**—Exactly as above, using $\frac{N}{100}$ silver nitrate. The better indicator here is sodium arsenate, owing to the great dilution. Calculate as NaCl.

12. **Determination of cyanides.** *Caution.—On no account risk sucking cyanide solution into a pipette. Deliver from a burette.*

When silver nitrate is added to an alkali cyanide (not *vice versa*) the following reactions take place:

$$(1)\ AgNO_3 + 2KCN = \underset{\text{(soluble)}}{KAg(CN)_2} + KNO_3.$$

When all the soluble cyanide has been converted into the complex salt, the next drop of silver solution reacts as follows:

$$(2)\ KAg(CN)_2 + AgNO_3 = KNO_3 + \underset{\text{(insoluble)}}{2AgCN},$$

and a *permanent* ppt. forms.

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Hence run $\frac{N}{10}$ $AgNO_3$ into the cyanide solution till a permanent ppt. is just obtained. Equation (1) is then just complete.

Since to form the complex salt $AgNO_3 = 2KCN$,

$$\therefore \ 1 \text{ c.c. } \frac{N}{10} AgNO_3 = \cdot 01302 \text{ gm. KCN}$$
$$= \cdot 0052 \text{ gm. (CN), and so on.}$$

B. Use of Ammonium Thiocyanate.

Silver thiocyanate is unaffected by dilute acids, so that if a soluble thiocyanate be added to a dilute acid solution of silver till pptn. is complete, the amount of silver can be calculated. The end of the reaction is shown by adding iron alum as indicator, the least excess of soluble thiocyanate giving the red colour of $Fe(CNS)_3$.

This method has the advantage that the silver solution need not be neutral. Hence the silver in alloys may be determined after solution in nitric acid, without having to render exactly neutral. The presence of other metals (except mercury) does not interfere, except in so far as coloured salts will make it impossible to see the end point.

1. **Preparation of $\frac{N}{10}$ ammonium or potassium thiocyanate.**—About 9 gms. of ammonium or 11 gms. of potassium thiocyanate are roughly weighed out and dissolved in the Giles flask to 1100 c.cs. 10 c.cs. of $\frac{N}{10}$ $AgNO_3$ are placed in a flask, 2 c.cs. of iron alum solution (saturated) added, and the thiocyanate is run in from a burette till a permanent red tinge is obtained. Calculate how much water to add to a litre of the thiocyanate to make it $\frac{N}{10}$.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiocyanate} = \cdot 010788 \text{ gm. Ag.}$$
$$1 \text{ c.c. } \frac{N}{10} AgNO_3 = 00761 \text{ gm. } NH_4CNS.$$

2. **Determination of silver in an alloy.**—Thoroughly clean a threepenny piece, wash with hot caustic soda solution, with dilute sulphuric acid, distilled water, dry and weigh. Dissolve in a little warm nitric acid (1 : 1) in a 250 c.cs. flask; make up to 250 c.cs. with water, shake and titrate 50 c.cs. at a time with $\frac{N}{10}$ thiocyanate and ferric indicator.

3. **Determination of halogens.**—Halides present in acid solution may be determined by pptg. with excess of $\frac{N}{10}$ silver solution, filtering from the ppt. in case of the chloride (unnecessary with bromide or iodide) and titrating the excess of silver with $\frac{N}{10}$ thiocyanate.

Filtration is necessary because $AgCl + NH_4CNS = NH_4Cl + AgCNS$ to some extent.

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When determining iodides by this method, the solution should be in a stoppered bottle. The silver nitrate is added gradually with thorough shaking, which avoids the enclosure of silver nitrate and of iodide by the silver iodide. Finally add ferric indicator and titrate the excess of silver as above.

C. Use of Normal Barium Chloride.

1. **Determination of sulphuric acid and sulphates.**—These may be determined in not too dilute solution by adding N. barium chloride till no more ppt. falls. The liquid is kept at the boil, and after each addition of the reagent the ppt. is allowed to settle before adding more. It is quite easy to see when no more ppt. forms, provided that the solution is not more dilute than normal.

In this way sulphates can be quickly determined with reasonable accuracy.

The solution should be treated with dilute hydrochloric acid before adding the barium solution if other acids are present which are pptd. by barium.

The reagent is made by dissolving 122·15 gms. of $BaCl_2$, $2H_2O$ (purest crystals) and making up to a litre.

$$1 \text{ c.c. N. } BaCl_2 = \cdot 04303 \text{ gm. } SO_4.$$

2. **Determination of chromic acid and chromates.**—By adding barium chloride to a solution of the chromate to which acetic acid and excess of sodium or ammonium acetate have been added, the orange colour of the solution will suddenly disappear and change to the much lighter lemon yellow of the ppt. of $BaCrO_4$ when sufficient barium solution has been added. It is better to use N. barium acetate as the reagent if it is available.

$$1 \text{ c.c. N. barium solution} = \cdot 058 \text{ gm. } CrO_4.$$

D. Use of Standard Uranyl Acetate.

1. **Determination of phosphoric acid.**—When uranyl acetate,

$$(UO_2)(C_2H_3O_2)_2,$$

is added to a phosphate, a pale greenish yellow ppt. of UO_2HPO_4 is formed. ($UO_2NH_4PO_4$ in presence of ammonium salts.)

The solution should be only slightly acid with acetic acid.

The end point is determined by withdrawing a drop of the solution on a glass rod and touching it on a drop of potassium ferrocyanide on a white tile. The least excess of uranyl salt gives a brown ppt. (or coloration) of uranyl ferrocyanide.

It is necessary to employ the uranyl solution against a solution of approximately the same strength and composition as the solution against which it was standardised.

Standardisation of the uranium solution.—About 39 gms. of uranium acetate are dissolved in water and made up to 1100 c.cs. in the Giles flask. The best substance to standardise the uranium upon is KH_2PO_4. 3·833 gms. (corresponding to 2 gms. of P_2O_5) are dissolved and made up to a litre. 50 c.cs. of this solution contain 0·1 gm. P_2O_5.

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To carry out the titration, 50 c.cs. are measured into a flask or beaker, and the uranium solution added till a drop of the liquid removed on a glass rod and touched on a drop of potassium ferrocyanide on a white tile gives a faint brown colour. Now heat the liquid to boiling and continue to add uranium solution till the brown colour is obtained again.

Note.—The reaction is only quantitative at the boil.

It is usual to make the uranium solution of such a strength that

$$1 \text{ c.c.} = \cdot 005 \text{ gm. } P_2O_5.$$

Under the above conditions, 50 c.cs. of the KH_2PO_4 solution should require 20 c.cs. of uranium solution. Calculate the amount of water to add and dilute in the usual way.

2. **Determinations of phosphoric acid** are made in an exactly similar manner, but the solution must be of approximately the same concentration as the phosphate against which the uranium was standardised. If mineral acids or their salts are present it is necessary to add 10 c.cs. of 10 % ammonium acetate solution to each volume to be titrated.

The most usual determinations of phosphoric acid are in phosphatic manures. In this case it is advisable to standardise the uranium against calcium phosphate.

The uranium solution for this purpose is usually made of such a strength that 1 c.c. represents 1 % of soluble phosphate (calculated as $Ca_3(PO_4)_2$), when 1 gm. of the fertiliser is taken for analysis. This is accomplished as follows:

Exactly 5 gms. of purest pptd. tri-calcium phosphate are dissolved in the minimum of dilute hydrochloric acid, ammonia added dropwise till a permanent ppt. just forms, and then excess of acetic acid. The whole is made up to a litre.

50 c.cs. of this solution = 0·25 gm. $Ca_3(PO_4)_2$.

The titration is carried out by taking 50 c.cs. of this solution, adding 10 c.cs. of 10 % ammonium acetate solution, running in uranium solution in the cold and finishing at the boil as already described. The uranium solution in the Giles flask is now diluted so that 25 c.cs. will be required for 50 c.cs. of the above solution.

Since 25 c.cs. = 0·25 gm. calcium phosphate, the number of c.cs. of uranium solution required will represent the percentage of soluble calcium phosphate when 1 gm. of a sample is taken for analysis.

3. **Determination of "soluble phosphate" in "superphosphate."**—Exactly 10 gms. of the sample are *gently* rubbed in a glass mortar with water till of the consistency and smoothness of cream. Wash into a 500 c.c. flask and continue the *gentle* rubbing and washing till it has all been transferred. Make up to 500 c.cs. Shake thoroughly for some time, filter through a *dry* filter into a *dry* vessel, rejecting the first few c.cs. of filtrate. Transfer 50 c.cs. (= 1 gm. of the sample) to a beaker, add ammonia till a permanent ppt. forms, redissolve in acetic acid, add ammonium acetate and titrate exactly as before. Repeat twice more.

1 c.c. uranium solution = 1 % "soluble phosphate."

Note.—If much iron or aluminium be present the above method is useless,

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as ferric and aluminic phosphates are insoluble in acetic acid. Gravimetric methods are necessary in this case (see pp. 212-3).

4. **Determination of the hardness of water** (*Clarke's method*).—The hardness is pptd. by a soap solution of known strength.

(i) *Preparation of the soap solution.*—Put 10-12 gms. of Castile soap into a litre flask and dissolve in 500 c.cs. of methylated spirit (redistilled industrial spirit). Make up to a litre and shake.

(ii) *Standardisation of the soap solution.*—Weigh out exactly 1 gm. of purest calcium carbonate (a clear *colourless* crystal of Iceland spar), dissolve it in dilute HCl in a basin covered with a clock-glass. Rinse the cover into the basin and evaporate dry on the water-bath. Repeat after adding some distilled water. Dissolve residue in distilled water, make up to a litre and shake.

1 c.c. contains the equivalent of 1 mgm. of $CaCO_3$.

To 15 c.cs. of this solution in a glass-stoppered bottle add 55 c.cs. of distilled water. Add the soap solution from a burette 1 *c.c at a time*, shaking thoroughly after each addition. When a lather which lasts for longer than 30 seconds is obtained, add the soap half a c.c. at a time, shaking as before. The titration is finished when a lather is obtained which lasts for two minutes. Repeat twice. Calculate how much to dilute the soap solution so that 10 c.cs. of the calcium solution will require 16 c.cs. of the soap solution.

[Experiment shows that 70 c.cs. of *distilled* water require 1 c.c. of the soap solution to give a permanent lather. Hence the extra c.c.]

(iii) *Determination of the hardness of water.*

(*a*) *Total hardness.*—Titrate 70 c.cs. of the water exactly as above. Subtract 1 c.c. from the volume of soap required. The result gives the number of grains per gallon of *total* hardness (say x).

(*b*) *Permanent hardness.*—Boil about 150 c.cs. of the water (counterpoised in a flask) for 20 minutes. Cool and make up to the original volume with distilled water. If a visible ppt. has formed, filter through a *dry* filter, rejecting the first few c.cs. Titrate 70 c.cs. as before and subtract 1 c.c. from the volume of soap. The result is the number of grains per gallon of permanent hardness (say y).

The temporary hardness is obviously $x - y$.

Note.—This method, though quick and convenient, is not scientifically accurate. The manner in which the soap solution is added makes a vast difference to the titration. Hence *always* add it in the same way and at the same rate.

To express the hardness on the French scale (parts per 100,000) use 100 c.cs. instead of 70 c.cs., and subtract 1·5 c.cs. from the burette readings.

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CHAPTER IV.

OXIDATION METHODS.

A. Use of $\frac{N}{10}$ Potassium Permanganate.

In presence of excess of sulphuric acid, the equation representing the oxidising action of permanganate is:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Thus 1 mol. of permanganate supplies 5 equivalents of oxygen.

Hence $\frac{N}{10}$ permanganate will contain $\frac{KMnO_4}{50} = 3{\cdot}16$ gms. per litre, corresponding to 0·8 gm. of available oxygen.

Anything quantitatively oxidised by permanganate in presence of sulphuric acid may thus be determined, the permanganate being its own indicator. The least excess is perceived by the permanent pink colour.

1. **Preparation and standardisation of the permanganate.**—If accuracy be desired it is better to standardise the solution, as even if the purest crystals obtainable be weighed out *exactly*, the solution will in the course of a few hours inevitably deteriorate owing to unavoidable introduction of organic dust, etc., which reduces it. If required at once (as in an examination) 3·16 gms. may be weighed out, dissolved and made up to a litre and regarded as $\frac{N}{10}$ for a short time.

Weigh out about 3·2 gms. of purest potassium permanganate. Grind in a glass mortar with 50 c.cs. of distilled water.* Allow to settle and pour the clear solution through a funnel into a litre flask (or take about 3·5 gms. and make up to 1100 c.cs. in a Giles flask). Continue till the whole has dissolved and been transferred. Finally make up to the mark, stopper, shake and leave 24 hours at least.

Standardise by one of the following methods:

(i) *With* $\frac{N}{10}$ *oxalic acid.*—Measure out 25 c.cs. of $\frac{N}{10}$ oxalic acid into a flask. Add 10 c.cs. of 4 N. sulphuric acid. Heat to about 90° and titrate with the permanganate till a permanent pink colour is obtained.

(*N.B.*—If a brown ppt. of hydrated manganese dioxide forms, insufficient sulphuric acid is present and the titration must be rejected.)

* Otherwise the solution of the crystals is very slow and tedious.

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Since $$H_2C_2O_4 + (O) = 2CO_2 + H_2O,$$

$$1 \text{ c.c. } \frac{N}{10} \text{ oxalic acid} = \cdot 00316 \text{ gm.} = 1 \text{ c.c. } \frac{N}{10}, KMnO_4.$$

Calculate and dilute in the usual way.

(ii) *By* $\frac{N}{10}$ *ferrous solution.*—

Use ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 . 6H_2O$.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

From the above equation 0·8 gm. oxygen oxidises 5 584 gms. of iron from ferrous to ferric state. Hence we make up an iron solution such that a litre contains 5·584 gms. of ferrous iron. This will be $\frac{N}{10}$ towards oxidising agents.

Weigh out exactly 3·921 gms. of purest ferrous ammonium sulphate. Dissolve in *cold freshly-boiled* approximately N. sulphuric acid, without shaking violently. Make up to 100 c.cs.

Titrate 25 c.cs. at a time with the permanganate. 25 c.cs. of $\frac{N}{10}$ permanganate will be required. Calculate and dilute as usual.

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 = \cdot 005584 \text{ gm. iron.} = 1 \text{ c.c } \frac{N}{10} \text{ ferrous solution.}$$

Note.—The ferrous solution cannot be kept.

(iii) *By* $\frac{N}{10}$ *thiosulphate.*—(See under this solution.)

The following may be determined by the use of $\frac{N}{10}$ $KMnO_4$.

2. **Determination of iron.**—If in the ferrous state determine just as described under standardisation by means of ferrous ammonium sulphate.

Note.—It is essential to avoid oxidation during solution of the substance. This can be done by dissolving in cold freshly-boiled dilute sulphuric acid.

In case of a substance, such as native ferrous carbonate, which requires heat to dissolve it, solution should be carried out in a graduated flask fitted with a bunsen valve, or with a delivery tube which dips into a beaker containing boiling dilute sulphuric acid. On cooling, the latter is drawn into the flask. The flow is stopped when the volume drawn in is just below the mark by closing a clip on the rubber connection. Cool before diluting to the mark.

Iron in iron wire, etc., cannot be accurately determined by means of permanganate, owing to the formation of unsaturated hydrocarbons, etc., during solution.

Chlorides may not be present except in very small amounts, owing to the oxidising action of permanganate on them.*

If the iron is in the ferric state it must first be reduced to ferrous :—

(*a*) *By nascent hydrogen.*—Sufficient separate aliquot parts of the solution having been placed in separate flasks, the reduction is performed by treating

* The effect of chlorides may be overcome by adding some manganous sulphate before titrating.

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with excess of 4N. sulphuric acid and adding pieces of pure zinc (foil best), till the solution gives no test for ferric iron (test a drop withdrawn on a glass rod with thiocyanate). Wait till any remaining zinc has dissolved. The method is slow and tedious.

(*b*) *By ammonium bisulphite.*—Prepare this as described on p. 28, Book I. Raise the ferric solution to the boil, and add the bisulphite slowly, boiling gently all the time till a slight excess is present. Add some dilute sulphuric acid till this excess has been destroyed. (Smell of sulphur dioxide disappears; test steam with litmus paper.) After cooling dilute to required volume with air-free water.

(*c*) *By hydrogen sulphide.*—Boil the solution in a flask fitted with a cork carrying two tubes, one reaching nearly to the bottom, the other just passing through the cork. Meanwhile pass hydrogen sulphide through the solution by attaching the longer tube to the kipp. When reduction is complete boil off excess of hydrogen sulphide in a current of carbon dioxide. (Test issuing steam with lead acetate paper.) Cool in the current of carbon dioxide and make up to required volume with boiled distilled water and sulphuric acid.

Ferrous and ferric iron together are determined by first titrating the ferrous iron, then reducing the whole to the ferrous state and titrating the total iron. The difference gives the ferric iron. Usually this determination will be with a mineral, as spathic ore. It must be very finely powdered in an agate mortar and dissolved as already described in dilute sulphuric acid with all precautions against oxidation.

3. **Determination of oxalic acid and oxalates.**—The titration is carried out as described under standardisation of permanganate by oxalic acid.

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 = \cdot 0044 \text{ gm. } C_2O_4$$
$$= \cdot 0045 \text{ gm. } H_2C_2O_4.$$

Iron and oxalic acid together, as in the determination of ferrous oxalate, may be determined by first titrating both the ferrous iron and the oxalic acid. The iron is then oxidised in another aliquot part of the solution by boiling and adding strong nitric acid dropwise till the dark brown colour disappears. The boiling is continued until the excess of nitrous acid is all driven off, cooled and the oxalic acid titrated. The difference between this and the total permanganate used gives that used for the iron.

4. **Determination of hydrogen peroxide.**

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

Titrate in the presence of sulphuric acid in the cold. From the equation we see that 1 c.c. $\frac{N}{10} KMnO_4 = \cdot 001701$ gm. H_2O_2.

5. **Determination of nitrites.**

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5NaNO_3.$$

As the sulphuric acid necessary cannot first be added to the nitrite owing to the instability of nitrous acid, and as the reaction in neutral solution is indefinite, the nitrite solution is delivered from the burette into a measured volume of permanganate to which sulphuric acid has been added. The

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most accurate results are obtained by adding the sulphuric acid gradually as the nitrite is added, keeping the acid in *slight* excess. Towards the end the reaction is rather slow, and the nitrite solution should be added slowly.

Indirect Determinations.

6. **Determination of calcium.**—The calcium is pptd. as oxalate. The ppt. is filtered, washed, decomposed with sulphuric acid and the free oxalic acid titrated.

The solution of the calcium salt is rendered alkaline with ammonia, acid with acetic acid, and raised to the boil. The calcium is pptd. by adding boiling ammonium oxalate drop by drop till in slight excess. Allow to settle, decant through a filter, and finally bring the ppt. on to the filter and wash with boiling water till the washings no longer react with calcium chloride solution or, after acidifying with sulphuric acid and heating, with one drop of $\frac{N}{10}$ permanganate.

Place the funnel in the neck of a graduated flask, make a small hole in the filter, and pour on to the ppt. hot dilute sulphuric acid. The ppt. must be completely washed off the filter. A little dilute hydrochloric acid may be used if necessary, but is not really desirable.

Finally cool, make up to the required volume with dilute sulphuric acid and titrate aliquot parts with permanganate at 80°-90°.

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 = \cdot 002003 \text{ gm. Ca.}$$

The determination may be otherwise carried out by pptg. the calcium with a *weighed* excess of ammonium oxalate exactly as described above. Filter, wash thoroughly, make up filtrate and washings to a known volume, and titrate the excess of ammonium oxalate with permanganate. Hence the weight that has reacted with the calcium is obtained.

7. **Determination of peroxides.**—Manganese dioxide, red lead, or lead peroxide will oxidise oxalic acid, thus:

$$MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2H_2O + 2CO_2.$$
$$Pb_3O_4 + 3H_2SO_4 + H_2C_2O_4 = 3PbSO_4 + 4H_2O + 2CO_2.$$

Weigh out about 0·35 gm. of finely-powdered pyrolusite. Transfer to a graduated 100 c.c. flask, together with either exactly 1·26 gms. of pure oxalic acid crystals ($H_2C_2O_4$, $2H_2O$) (equivalent to 100 c.cs. of $\frac{N}{10}$ oxalic acid) or 10 c.cs. of (accurately) N. oxalic acid, and a sufficient excess of sulphuric acid. Heat gently on a sand-bath till the reaction is complete (evolution of CO_2 ceases), cool, make up to 100 c.cs. and titrate the excess of oxalic acid with $\frac{N}{10}$ permanganate in an aliquot part.

$$1 \text{ c.c. } \frac{N}{10} H_2C_2O_4 = \cdot 004347 \text{ gm. } MnO_2.$$
$$= \cdot 03428 \text{ gm. } Pb_3O_4.$$
$$= \cdot 01196 \text{ gm. } PbO_2.$$

Amounts of red lead or of lead dioxide should be weighed out corresponding to the weight of manganese dioxide recommended.

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8. **Determination of persulphates.**

$$K_2S_2O_8 + 2FeSO_4 = K_2SO_4 + Fe_2(SO_4)_3.$$

Treat a weighed amount of the persulphate with about twice as much $\frac{N}{10}$ ferrous solution as is necessary for the above reaction. Add some freshly-boiled dilute sulphuric acid (4N) and boil in a current of carbon dioxide for 10 minutes. Cool, make up to a known volume with cold boiled dilute sulphuric acid and titrate an aliquot part with permanganate. The excess of ferrous iron is thus determined, and hence the amount used in the above reaction.

$$1 \text{ c.c. } \frac{N}{10} \text{ ferrous solution} = \cdot 009707 \text{ gm. } H_2S_2O_8.$$
$$= \cdot 013516 \text{ gm. } K_2S_2O_8.$$
$$= \cdot 01141 \text{ gm. } (NH_4)_2S_2O_8.$$

9. **Determination of percarbonates.**—If a percarbonate is treated with cold very dilute sulphuric acid,

$$K_2C_2O_6 + 2H_2SO_4 = 2KHSO_4 + 2CO_2 + H_2O_2.$$

The hydrogen peroxide is titrated with permanganate as already described.

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 = \cdot 00991 \text{ gm. } K_2C_2O_6.$$

B. Use of $\frac{N}{10}$ Potassium Dichromate.

Potassium dichromate in acid solution oxidises as follows:

$$K_2Cr_2O_7 + 8HCl = 2CrCl_3 + 2KCl + 4H_2O + 3O.$$

Hence one molecule supplies six equivalents of oxygen. $\frac{N}{10}$ dichromate therefore will contain $\frac{K_2Cr_2O_7}{60} = 6 \cdot 570$ gms. Exactly this weight of the finely ground purest salt obtainable is transferred to a litre flask, dissolved in some *hot* water, and after solution is complete, made up to 1000 c.cs.

As dichromate can be obtained in as pure a state as the substance used to standardise it, this process will be unnecessary. It may, however, be standardised by ferrous ammonium sulphate if desired, or by $\frac{N}{10}$ thiosulphate (*q.v.*).

Owing to the green colour of the chromium salt produced on reduction of the dichromate, it cannot act as its own indicator.

As dichromate is chiefly used for determining iron, we employ an outside indicator, viz. potassium ferricyanide. Drops of this solution are treated from time to time with a drop of the solution being titrated. As long as any ferrous salt is left, a blue colour will be produced, but as soon as the oxidation is complete, the brown colour of ferric ferricyanide is obtained.

1. **Determination of iron in haematite.**—About two grams of the very finely-powdered mineral are transferred by means of a funnel to a 250 c.c. flask. Hot strong hydrochloric acid is dropped slowly into the funnel to wash into the flask all traces of the mineral. About 70 c.cs. of the acid are now

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added and the flask heated on a water-bath till solution is complete. (The addition of a gram of stannous chloride facilitates the solution.) The ferric chloride is now reduced to the ferrous state by means of stannous chloride. An aliquot part is heated to about 80° and stannous chloride solution is run in from a burette,* half a c.c. at a time, till the solution is colourless. Excess of stannous chloride is now destroyed by adding several c.cs. of mercuric chloride, after which it is titrated with $\frac{N}{10}$ dichromate until a drop of the liquid, withdrawn on a glass rod and placed in contact with a drop of potassium ferricyanide on a tile, no longer gives a blue colour.

Students are apt to have difficulty at first with this most accurate method. A few of the errors into which they fall are here described in detail.

(1) The ferricyanide solution must contain no trace of ferrocyanide, which gives a blue colour with ferric salts. Hence thoroughly wash a crystal of ferricyanide with distilled water before dissolving it. Dust, etc., will reduce ferricyanide to ferrocyanide.

(2) The tile on which the drops of indicator are placed should be scrupulously clean for similar reasons.

(3) The glass rod with which drops of the solution are withdrawn from the vessel must be washed under the tap after every test.

(4) Care should be taken, if the titration is done in a flask, that none of the solution is left on the neck of the flask in withdrawing a test drop. Otherwise some ferrous salt will inevitably be left there, and there is danger of continuing to carry out some of it on the rod long after the titration is really finished.

(5) Anything more than a *very small* excess of stannous chloride must be avoided, or there is danger that insufficient mercuric chloride will be added to destroy it, as this salt is not very soluble in water.

$$1 \text{ c.c. } \frac{N}{10} K_2Cr_2O_7 = \cdot 005584 \text{ gm. Fe.}$$

Note.—Stannous chloride is by far the most convenient reducing agent for ferric salts. It cannot be used for permanganate because of introducing hydrochloric acid. The presence of this, however, does not affect the dichromate.

2. **Determination of iron in iron wire, etc.**—About 0·5 gram of iron wire, free from rust, is dissolved in excess of hydrochloric acid in a 100 c.c. flask, with suitable precautions against oxidation as described under permanganate, p. 248. After making up to 100 c.cs. with air-free water, 25 c.cs. at a time are titrated with $\frac{N}{10}$ dichromate, as already described.

3. **Ferrous iron in the presence of ferric iron** is determined similarly to the method used for its determination with permanganate, p. 248, except that stannous chloride may be used as the reducing agent.

C. Use of $\frac{N}{10}$ Ferrous Solution.

Anything that oxidises ferrous salts quantitatively to ferric salts may be

* By adding the reducing agent from a burette, care is only necessary for the first portion. Other aliquot parts may be treated at once with the required volume.

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determined by allowing excess of $\frac{N}{10}$ ferrous solution to act upon it and determining the excess of ferrous salt by means of $\frac{N}{10}$ dichromate. These methods are little used, however, because:

(*a*) Standard ferrous solution cannot be kept.

(*b*) Other methods are available which are more easily carried out.

Two determinations only are here described.

1. **Determination of chromic acid and chromates.**—The solution of the chromic acid or chromate in dilute sulphuric acid is treated with excess of freshly-prepared $\frac{N}{10}$ ferrous ammonium sulphate and the excess titrated with $\frac{N}{10}$ $K_2Cr_2O_7$.

$$1 \text{ c.c. } \frac{N}{10} \text{ ferrous solution} = \cdot 003333 \text{ gm. } CrO_3$$
$$= \cdot 003867 \text{ gm. } CrO_4.$$

2. **Determination of chromium in chromite.**—About 0·5 gm. of the *very finely-powdered* mineral is thoroughly mixed in a platinum crucible with about 4 gms. of a mixture of 1 part potassium chlorate and 3 parts of fusion mixture and heated over the blowpipe for 20 minutes. Dissolve the product in hot water, boil, cool and add hydrochloric acid to dissolve the iron oxide. Dilute to 100 c.cs. in a graduated flask, and to 25 c.cs. add excess of $\frac{N}{10}$ ferrous solution. Titrate the excess with $\frac{N}{10}$ dichromate.

$$1 \text{ c.c. } \frac{N}{10} \text{ ferrous solution} = \cdot 001733 \text{ gm. Cr.}$$

3. **Valuation of zinc dust.**

$$3Zn + K_2Cr_2O_7 + 7H_2SO_4 = 3ZnSO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Weigh out about 0·5 gm. of zinc dust, transfer to a 250 c.c. flask, and add 100 c.cs. of $\frac{N}{5}$ $K_2Cr_2O_7$. Render strongly acid with sulphuric or hydrochloric acid, and when the action is complete dilute to 250 c.c. with distilled water. Run this solution from a burette into 10 c.cs. of $\frac{N}{10}$ ferrous solution and thus determine the amount of dichromate left. From the amount used by the zinc the weight of zinc in the sample can be calculated.

$$1 \text{ c.c. } \frac{N}{5} K_2Cr_2O_7 = \cdot 006537 \text{ gm. zinc.}$$

D. Use of $\frac{N}{10}$ Iodine and $\frac{N}{10}$ Sodium Thiosulphate.

A solution of iodine (best in potassium iodide solution) reacts quantitatively with thiosulphate as follows:

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

The end of the reaction is seen by the disappearance of the colour of the iodine solution, or more accurately by using some starch solution as indicator, the blue iodide of starch acting on thiosulphate in the same way as free iodine.

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Hence anything which either:

(*a*) Oxidises hydriodic acid quantitatively to iodine, or

(*b*) Is oxidised quantitatively by iodine, can be determined.

1. **Preparation of the solutions.** (*a*) $\frac{N}{10}$ **Iodine,** I = 126·92.—Exactly 12·692 gms. of chemically pure iodine are weighed out in a stoppered weighing bottle, and transferred to a litre flask, washing out the weighing bottle several times with potassium iodide solution. 25 gms. of potassium iodide in 100 c.cs. of water are now added, and the flask shaken thoroughly till all the iodine has dissolved. This usually takes some time. Then make up to a litre with freshly-boiled cold distilled water and shake well. Preserve in a well-stoppered bottle in a cool, dark cupboard.

(*b*) $\frac{N}{10}$ **Thiosulphate,** $Na_2S_2O_3, 5H_2O = 248·2$.—Thiosulphate cannot generally be obtained chemically pure. Hence weigh out roughly 28-29 gms., dissolve in cold freshly-boiled distilled water in the 1100 c.c. Giles flask, and titrate against the $\frac{N}{10}$ iodine, using starch solution as indicator. (Do not add the starch solution till the colour of the iodine is pale straw-colour.) Calculate and dilute to $\frac{N}{10}$ as usual. Preserve in the dark in well-stoppered bottles.

Iodine solution prepared and kept as above keeps well, but the thiosulphate should be frequently re-titrated.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = ·012692 \text{ gm. iodine.}$$

(*c*) **Preparation of the starch solution.**—About a gram of the best potato starch is made into a thin cream with a few c.cs. of water and poured into 100 c.cs. of boiling water. Filter and use at once. About 5 c.cs. should be used for each titration. It is more convenient to use one of the forms of "soluble starch" which are now on the market.

Other Methods of standardising thiosulphate.

The methods now to be described are exceedingly accurate, and if desired it is well to standardise the thiosulphate thus and to use it to standardise the iodine.

2. **By** $\frac{N}{10}$ $K_2Cr_2O_7$ **or** $KMnO_4$.—25 c.cs. of $\frac{N}{10}$ $K_2Cr_2O_7$ or $KMnO_4$ are run into about 25 c.cs. of 5 % potassium iodide solution, and acidified strongly with acetic or dilute hydrochloric acid. An amount of iodine is thus liberated corresponding to 25 c.cs. of $\frac{N}{10}$ iodine. Titrate with the thiosulphate, adding starch solution towards the end of the reaction.

Remember that the solution, when dichromate is used, will be green at the finish.

3. **By** $\frac{N}{10}$ **potassium bi-iodate.**—This salt is readily obtained in a high

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state of purity. On adding to potassium iodide and rendering acid, the following reaction occurs:

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

Hence 1 mol. of the salt liberates 12 equivalents of iodine.

Therefore weigh out $\frac{KIO_3, HIO_3}{120} = 3{\cdot}2496$ gms., dissolve in water and make up to a litre.

25 c.cs. of this solution, added to 25 c.cs. of 5 % potassium iodide and acidified with acetic or dilute sulphuric acid, liberates iodine equivalent to 25 c.cs. of $\frac{N}{10}$ iodine.

Titrate with the thiosulphate to be standardised.

Estimations by means of $\frac{N}{10}$ thiosulphate.

4. **Determination of strength of chlorine or bromine water.**—A measured volume (5 c.cs. usually sufficient) is run from a burette into 20 c.cs. of 5 % potassium iodide and titrated with $\frac{N}{10}$ thiosulphate, using starch solution as usual.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = {\cdot}003546 \text{ gm. chlorine}$$
$$= {\cdot}007992 \text{ gm. bromine.}$$

5. **Valuation of bleaching powder.**—About 10 gms. are accurately weighed from a weighing bottle, transferred to a mortar and ground up with 50 c.cs. of water. Allow to settle somewhat and pour the milky liquid into a litre flask. Continue the grinding and decanting with more water till the whole is transferred to the flask. Make up to 1000 c.cs. and shake.

Transfer 25 c.cs. to a flask containing 20 c.cs. of 5 % potassium iodide, and render acid with acetic acid. The liberated chlorine turns out an equivalent amount of iodine from the iodide, which is titrated in the usual way with $\frac{N}{10}$ thiosulphate.

Calculate the percentage weight of "available chlorine" in the specimen.

In case of a poor specimen it may be necessary to take 50 c.cs. for each titration.

Note.—The flask containing the solution of bleaching powder should be thoroughly shaken immediately before the aliquot part is withdrawn, and the milky liquid is pipetted out. It should *not* be allowed to settle.

Other hypochlorites are similarly estimated.

6. **Determination of chromic acid and chromates.**—These are determined just as described under standardisation of thiosulphate by dichromate.

7. **Valuation of pyrolusite.**—About ·5 gm. of pyrolusite, finely powdered, is transferred to the flask shown in Fig. 58, by means of a funnel and a little cold concentrated hydrochloric acid. In the flask a few grams of magnesite (native) have been previously placed, and in the two U-tubes potassium iodide solution. The first U-tube contains about 2·5 gms. of iodide in 15 c.cs. of water, the second one about 15 c.cs. of 5 % iodide. The level of the

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solutions in each should not be higher than shown in the sketch. The U-tubes are cooled in water to prevent volatilisation of the iodine.

The flask is immediately connected to the apparatus by the ground-in joint, and heated on a gauze with a *small* flame. The evolution of chlorine should not be too rapid. The magnesite supplies a gentle stream of carbon dioxide throughout the process, which sweeps all the chlorine out of the flask. When the action is over boil the contents of the flask for a few minutes

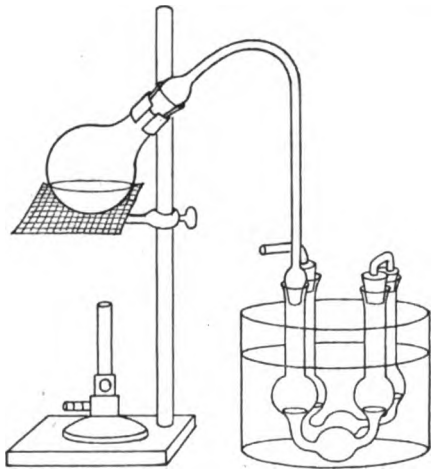

FIG. 58.

to drive all chlorine out of solution. Rinse the U-tubes into a 100 c.c. flask, washing them several times. Finally make up to 100 c.cs. and titrate the liberated iodine with $\frac{N}{10}$ thiosulphate.

Since $MnO_2 = Cl_2 = I_2$,

$$\therefore \text{ 1 c.c. } \frac{N}{10} \text{ thiosulphate} = \cdot 004346 \text{ gm. } MnO_2.$$

Other peroxides may be similarly determined if they react quantitatively with hydrochloric acid.

8. **Determination of copper.**—In the absence of other substances acting on potassium iodide, copper may be determined by the following reaction:

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$

Weigh out about 2 gms. of copper sulphate. Dissolve and make up to 100 c.cs. Add 25 c.cs. at a time to 20 c.cs. of 5 % iodide and titrate with $\frac{N}{10}$ thiosulphate without filtering, using starch as indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = \cdot 006357 \text{ gm. of copper.}$$

Note.—The reaction at the end is rather slow, owing to the fact that CuI_2, first formed, does not decompose completely in the presence of iodine (mass action), and the blue colour reappears after it has disappeared, the time

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for reappearance becoming longer progressively. Hence, for the highest accuracy the thiosulphate for this determination should be "standardised" against pure copper sulphate, and the disappearance of the blue colour for a definite period, say 1 minute, taken as the end, both in standardising and estimating.

9. **Ferric chloride** may be similarly determined, but the completion of the reaction is very tedious and the method is not recommended. It saves reduction to the ferrous state, however, necessary with permanganate and dichromate.

10. **Determination of dissolved oxygen in water (Winkler's method)**, *Rideal and Stewart*, Analyst, xxvi. 141.—This estimation is one of the methods adopted in water-analysis. If the dissolved oxygen is below the normal, contamination with organic matter may be suspected.

The principle is to treat the water with manganous hydroxide, which is oxidised by the dissolved oxygen to MnO_2. This on treatment with KI and HCl sets free an equivalent amount of iodine, which is titrated with $\frac{N}{10}$ thiosulphate.

A stoppered bottle of about 300 c.cs. capacity (accurately determined) is filled with the water and 1 c.c. of a 40 % solution of manganous chloride (free from iron) is introduced to the bottom of the bottle by a long-stemmed pipette. This is followed by 3 c.cs. of a 32 % solution of pure caustic soda, which contains 10 % of potassium iodide.

The stopper is put in (no air to be included) and the contents thoroughly mixed, shaken, and allowed to stand till the ppt. has settled. Now add 3 c.cs. of pure concentrated hydrochloric acid by means of the pipette. Again stopper the bottle and shake. Set aside for 5 minutes and finally titrate the liberated iodine in the usual way.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = \cdot 0008 \text{ gm. oxygen.}$$

Use of $\frac{N}{10}$ Iodine.—It is to be noted that most oxidations with iodine are more or less incomplete if theoretical quantities are taken, owing to the reverse action taking place. This makes the reaction very slow at the end, and it is quicker in nearly every case, besides being more accurate, to add excess of iodine and titrate the excess with thiosulphate.

If desired, however, most of the following may be titrated with iodine, first adding starch solution. The appearance of a permanent blue colour is taken as the end-point.

11. **Determination of sulphurous acid.**—Here it is *necessary* not only to use excess of iodine, but to add the sulphurous acid to the iodine, *not vice versa.*

Usually the acid will require diluting to approximately $\frac{N}{10}$ strength. A rough trial may first be made. Finally run an aliquot part of the diluted solution into excess of $\frac{N}{10}$ iodine, add starch solution and titrate the excess with thiosulphate.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = \cdot 004104 \text{ gm. } H_2SO_3$$
$$= \cdot 004003 \text{ gm. } SO_2.$$

Sulphites may be similarly determined.

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12. **Determination of hydrogen sulphide in solution.**—This may be titrated with $\frac{N}{10}$ iodine and starch solution.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = \cdot 001704 \text{ gm. } H_2S.$$

13. **Determination of arsenic.**—Arsenious acid is oxidised by iodine to arsenic acid.

$$H_3AsO_3 + I_2 + H_2O = 2HI + H_3AsO_4.$$

This reaction is reversible in acid solution, and alkali must not, of course, be present. Hence the titration is performed in the presence of excess of sodium bicarbonate, *e.g.*

Valuation of As_2O_3.—Weigh out about 1·2 gms. of the specimen and dissolve it in the minimum of caustic soda solution in a 250 c.c. flask. Render acid with dilute hydrochloric acid, having added a drop of phenolphthalein as indicator. Now add a cold saturated solution of sodium bicarbonate till present in some excess. If the red colour of the phenolphthalein reappears, add $\frac{N}{10}$ acid till it is *just* decolorised. (Most specimens of bicarbonate contain traces of the normal carbonate.) Finally make up to 250 c.cs. and titrate 25 c.cs. at a time with $\frac{N}{10}$ iodine, or *better*, add excess of iodine and titrate back with thiosulphate.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = \cdot 004948 \text{ gm. } As_2O_3$$
$$= \cdot 003748 \text{ gm. As.}$$

14. **Determination of antimony.**—Antimony in the *-ous* state may be determined in a precisely similar manner to that described for arsenic, and the same observations apply to the reaction.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = \cdot 00721 \text{ gm. } Sb_2O_3$$
$$= \cdot 00601 \text{ gm. Sb.}$$

The antimony in tartar emetic may be determined as an example. Dissolve a suitable quantity in water, add some excess of bicarbonate (rendered exactly neutral to phenol-phthalein as before, if necessary). Titrate with iodine, or excess of iodine and thiosulphate.

E. Use of $\frac{N}{10}$ Arsenious Acid.

Substances which oxidise arsenious acid quantitatively to arsenic acid may be determined by its use. As indicator strips of filter paper dipped in a starch and potassium iodide solution and dried are used. The arsenious acid solution is prepared from pure As_2O_3, and standardised if necessary, exactly as described under the estimation of arsenic, p. 258.

EXAMPLES.

1. **Determination of bleaching powder.**—The bleaching powder, dissolved as described on page 255, is titrated with the arsenious acid in presence of

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excess of sodium bicarbonate, which should be added to each aliquot part as necessary. From time to time a drop is withdrawn on a glass-rod and brought on to a strip of the starch-iodide paper. When a blue colour no longer appears the hypochlorite has all been destroyed and the reaction is finished.

$$1 \text{ c.c. } \frac{N}{10} \text{ arsenious acid} = \cdot 003546 \text{ gm. available chlorine.}$$

2. **Determination of chlorine or bromine water.**—Either of these may be directly titrated with arsenious acid. The addition of bicarbonate is unnecessary in these cases. The indicator is used as in the previous experiment.

$$1 \text{ c.c. } \frac{N}{10} \text{ arsenious acid} = \cdot 003546 \text{ gm. Cl.} = \cdot 007992 \text{ gm. Br.}$$

Note.—The use of $\frac{N}{10}$ arsenious acid may mean the saving of much time on occasion, as by using purest resublimed As_2O_3 it can be prepared in a few minutes. If iodine and thiosulphate are not at hand, their preparation and standardisation take some time.

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CHAPTER V.

COLORIMETRIC METHODS.

THIS method, which is used chiefly for estimating *small amounts* of substances which give strongly coloured solutions, consists in matching the depth of tint of the liquid to be estimated with that of a standard liquid. It is a great advantage, though not absolutely necessary, to have an instrument which by a suitable optical arrangement shows the two tints side by side in the same field of view.

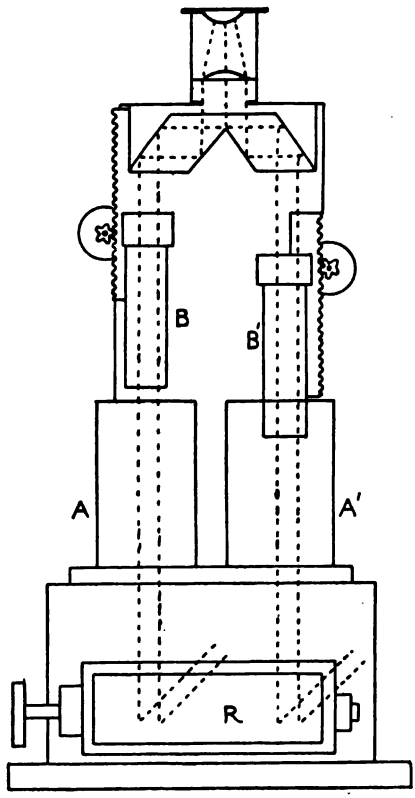

FIG. 59.

Dubosq's colorimeter is here described (Fig. 59).

The vessels *A*, *A'* contain the liquid under examination and the standard with which it is to be compared. By lowering or raising tubes *B*, *B'* the depths of liquid through which the light travels can be altered. When the tints match, the two concentrations are obviously inversely proportional to the depths of liquid.

The reflector *R* must be evenly illuminated by diffused light, and the rays of light are reflected into the eyepiece as shown, the beam passing through each liquid affecting half the field of view.

To use the instrument, put some of the standard liquid in *A*, and some of the liquid to be examined in *A'*. There should not be so much of either liquid as to cause it to overflow when *B* and *B'* are lowered to the bottom of *A* and *A'*.

The zero is now found by lowering *B* and *B'* to the bottom of *A* and *A'* and reading the verniers. Then raise *B* to a suitable height (the tint should

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not be too deep nor too pale; each observer will suit himself) and then B' is raised till the tints match. The verniers are again read. Repeat several times, and again repeat with B at different heights.

If c is the concentration of the substance in the standard, c' that in the liquid being examined, and d and d' are the respective depths of liquids which match in tint, then

$$\frac{c'}{c} = \frac{d}{d'}$$

$$\therefore\ c' = \frac{cd}{d'}.$$

The following determinations may be made by the colorimeter.

Ammonia.—The nitrogen present as ammonia in sewage or natural water is estimated thus. The reagents required are:

(i) *Nessler's reagent.*—To a cold solution of mercuric chloride of known strength add exactly the required amount of potassium iodide to ppt. HgI_2 completely. Allow to settle, decant, wash the ppt. several times with a little distilled water and then dissolve in the correct quantity of potassium iodide. Excess of alkali is then added. Suitable quantities are:

$HgCl_2$ - -	12 gms. in 100 c.cs. of water.
KI - -	Two lots of 7·4 gms. each.
KOH - -	15 gms in 15 c.cs. of water.

Finally dilute to about 200 c.cs. and set aside. Decant into a clean bottle and preserve in the dark.

(ii) *Standard ammonia solution.*—Dissolve exactly 3·1365 gms. of pure dry NH_4Cl and make up to a litre with ammonia-free water. Dilute 10 c.cs. of this to a litre with the same water.

1 c.c contains 0·01 mgm. of NH_3.

(iii) *Ammonia-free water.*—Distil spring or distilled water with a little pure sodium carbonate (heated). Reject the first quarter and test the rest of the distillate from time to time with Nessler's reagent till no colour is apparent after 10 minutes. Collect in a clean bottle and preserve for use. (Do not continue the distillation to dryness.)

The estimation is carried out by stirring and shaking a suitable amount of the water to be tested with 2 c.cs. of saturated soda solution. A suitable quantity of this is transferred to the colorimeter vessel, and mixed thoroughly with 2 c.cs. of Nessler's reagent. 5 c.cs. of the standard ammonium solution are diluted to a known volume (say 100 c.cs.) treated with the soda and Nessler as above and placed in the other vessel. After standing for 10 minutes the tints are matched.

Note.—(i) The colour of the solution being estimated should not be much darker than the standard ammonia solution. If this is the case then less water must be taken for the determination. On the other hand, if the colour is very faint it may be necessary to concentrate some of the water (50 c.cs. are distilled off after adding 2 c.cs. of the soda solution).

(ii) For all dilutions, etc., ammonia-free water must be used.

For further particulars of this method, see treatises on Water Analysis.

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Nitrites (employed for nitrites in drinking water, etc.).—*Griess-Ilosvay method* (Warington, *J.C.S.*, 1881, 231).

Reagents.—(i) Dissolve half a gram of sulphanilic acid in 150 c.cs. of dilute acetic acid.

(ii) Dissolve 0·1 gm. α-naphthylamine in a little strong acetic acid and the colourless solution mixed with 130 c.cs. of dilute acetic acid.

(iii) *Standard nitrite solution.*—Pure $NaNO_2$ is dissolved in pure water so that 1 c.c. contains ·01 mgm of N_2O_3.

Compare the tints of solutions containing

(*a*) 10 c.cs. of the standard, 1 c.c. each of the reagents, in 100 c.cs. of solution.

(*b*) A suitable amount of the liquid to be tested and 1 c.c. each of the reagents, in 100 c.cs. of solution.

Note.—Colour should not be developed for at least a minute or the solution is too strong. Leave for 20 minutes before testing.

Cobalt (*Skey's method.* See Mellor, *Tr. Eng. Cer. Soc.*, 1908, **8**, 132).—The colour of $Co(CNS)_2$ produced on adding NH_4CNS to a cobalt salt and extracting with a mixture of alcohol and ether is made use of.

The standard solution of cobalt sulphate contains 0·1 mgm. of cobalt per c.c. A suitable amount is taken, acidified with a few drops of dilute sulphuric acid and a mixture of alcohol and ether added and shaken. Compare the tint with that of the solution being examined, which is treated similarly. *Iron must be absent.*

Copper (Carnelly, *C.N.*, xxxii. 308).—The purple-brown colour obtained when potassium ferrocyanide is added to very dilute copper solutions is employed. (One must be quite certain that the colour is wholly due to copper !)

Standard solution.—Dissolve 0·395 gm. of pure $CuSO_4$, $5H_2O$ in a litre of solution. 1 c.c. = 0·1 mgm. Cu.

Reagents.—10 % solution of ammonium nitrate.
4 % solution of potassium ferrocyanide.

Place 5 drops of the ferrocyanide in a graduate, add 150 c.cs. of water and 10 c.cs. of the standard solution.

Treat a measured amount of the solution to be examined (which must be exactly neutral) in the same way. Compare the tints.

Iron (Thomson, *J.C.S.*, 1885, 493).—Suitable for iron in mineral waters, etc.

Standard solution.—0·7 gms. of pure ferrous ammonium sulphate is dissolved in water, acidified with dilute H_2SO_4, oxidised by adding pure chlorine water till present in slight excess, boiling off the chlorine and diluting to a litre. 1 c.c. = 0·1 mgm. of iron.

The solutions are prepared for matching by placing 5 c.cs. of dilute HCl, 15 c.cs. of dilute ammonium thiocyanate and a suitable amount of the solutions of iron in each of two vessels. Dilute to 100 c.cs. (or other convenient volume) and match the tints.

Other substances determined for technical purposes by colour methods are **titanium, chromium, carbon in steel,** etc., for which technical works may be consulted.

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It must be borne in mind that all colour estimations are accurate only when it is absolutely certain that all the colour is due to the substance being determined.

Many chemists do not use a colorimeter for the above estimations, preferring to make an equal volume of standard solution of the same tint as the solution being examined. This involves the preparation of several such solutions, whereas one only is necessary if a colorimeter is available.

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PART IV.

GAS ANALYSIS.

CHAPTER I.

ABSORPTION METHODS.

Two methods are in general use for the analysis of gases.

(1) **Absorption methods,** in which the gas to be determined is absorbed in a suitable reagent and the diminution in volume measured.

(2) **Combustion methods,** in which a combustible gas is burnt or sparked with excess of oxygen and its volume (or its formula, if that is being sought) determined from the changes in volume that take place.

In addition to these methods, many substances are determined by measuring the volume of gas evolved in some reaction, *e.g.* nitric acid by causing it to act on mercury and measuring the nitric oxide evolved. These methods, which are not strictly gas analyses, but analyses by means of gas measurements, are known as **gasometric determinations.**

Absorption methods.—There are numerous designs of apparatus on the market for the measurement and absorption of gases. Three only will be described here, viz,, those of **Bunte, Hempel and Tollen,**

A. **The Bunte gas burette** is very simple in construction and in use, and the same vessel serves both for measuring the gases and treating them with absorbents. With care and practice results quite as accurate as with more elaborate apparatus are obtained, and in addition the burette itself may be used with other absorption apparatus, such as Hempel's and Dreschmidt's pipettes, if desired.

The burette and the suction bottle used with it are shown in Fig. 60. The graduated portion holds about 110 c.cs., the zero mark being in the position shown. It is customary to take exactly 100 c.cs. of gas for analysis, and the decreases in volume are then read directly and give the volume percentages of the constituents without further calculation. It should be noted that all measurements are assumed to be made at the same temperature and pressure.

Filling the burette.—Connect a funnel to *F* by means of a long rubber tube. Raise the funnel, open tap *E*, and turn *D* so that *A* is connected to *C*. Pour water into the funnel till the burette and the bore of the tap and capillary *C* are full of water. Carefully remove all air bubbles. Now connect *A* and *B* and by raising the funnel suitably, fill *B* to the mark. To fill the burette with

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gas connect C to the source of gas by a thick-walled capillary tube filled with water. Connect C and A, open E and lower the funnel till about 105 c.cs. of gas have been drawn in. Now close both taps and remove the funnel and rubber tube.

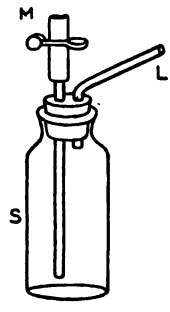
The gas in this burette is always measured at a pressure equal to that of the atmosphere + the column of water in B. To measure exactly 100 c.cs. of gas at this pressure, proceed as follows:

Water is put in the suction bottle S, and by opening the cork and blowing into L, the tube and the rubber connection are completely filled with water. Now connect M to F, open F and M, and by blowing into L and carefully squeezing the pinch cock M, bring the water level in the burette to zero. Close M.

We have now 100 c.cs. of gas at room temperature, but at a pressure above the required pressure. To attain this pressure, M is cautiously opened until the water level in B is *about* 0·2 c.cm. below zero. Close M, and by turning tap D connect A with B. The excess of gas bubbles out through the water in B, and *a small quantity of water from B enters A*. This is the reason for taking 100·2 c.cs. of the gas at the higher pressure. If the exact small excess volume has been properly judged, the water level will now stand exactly at zero.

This small allowance will only be found, of course, after a few preliminary trials, but once found there is no further trouble. With most Bunte burettes it is exactly 0·2 c.cm.

Note.—Before reading the volume in any gas burette where water is the confining liquid, a definite time should always be allowed for the burette to drain. Three minutes is a suitable time, and is readily measured with an ordinary "egg-boiler" sand-glass. Turn the glass immediately the pressure is adjusted, and as soon as the sand has run out, take the reading. The necessity for this can easily be shown by a trial.



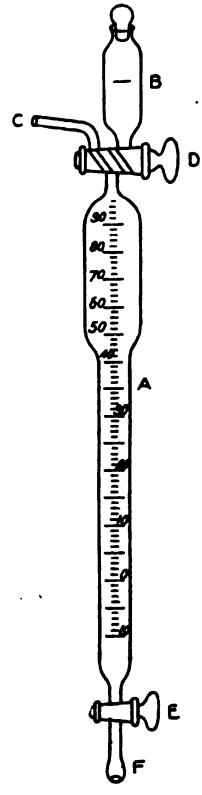


FIG. 60.

The gas in the burette is now ready for analysis.

To introduce an absorbent.—First suck the water out of the burette by connecting to the suction bottle as before and sucking at tube L, opening M and E. Do not allow gas to enter the bore of the tap E; close E. Remove the bottle, dip F into some of the reagent in a basin, and on opening E the reagent is drawn into the burette. Close E, and holding the burette horizontally by B and F, with the thumbs on the taps to prevent them from falling out, gently shake the reagent for 5 or 10 minutes.

On no account warm the burette itself by holding it in the hand.

When absorption is complete, remove the reagent by means of the suction

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bottle and close *E*. Rinse the reagent from the walls of the burette by cautiously opening *D* and allowing a little water to flow down. Remove this as before and repeat. Close *D* and fill *B* to the mark with water. Dip *F* under water in a basin and open *E*. Finally close *E*, connect *A* and *B* for a moment and leave burette to drain for 3 minutes. Read the volume.

Other absorbents are introduced similarly, save that as the volume of the gas gets less it *may* become necessary to withdraw the water or reagent from the burette by means of the filter-pump. This, however, must be used cautiously, being attached to tube *L* of the suction bottle.

N.B.—In analysing gases containing carbon dioxide, water saturated with carbon dioxide must be used as the confining liquid until the carbon dioxide has been absorbed. It is then replaced by distilled water.

Absorbents.—The reagents used for absorbing various gases are shown below.

Carbon dioxide.—Caustic potash (1 part in 2 of water).

Oxygen.—Sodium hyposulphite, $Na_2S_2O_4$ (very slightly alkaline),
or Solid phosphorus (sticks in special pipette),
or Alkaline pyrogallol solution,
or Chromous chloride.

The last named is very tiresome to prepare and use, but it is necessary only when hydrogen sulphide is present.

Carbon monoxide.—Dissolve 10 gms. of cupr*ous* chloride in a little saturated ammonium chloride solution and dilute to 50 c.cs. with strong ammonia. (This reagent also absorbs oxygen.) Its absorptive power for carbon monoxide is not very large. (The above quantities will absorb with certainty about 15 c.cs. of CO per c.c.)

Ethylene, acetylene, and homologues.—Bromine water.

Benzene and toluene vapours.—Bromine water.

Note.—Usually the gases absorbed by bromine water are grouped together as "heavy hydrocarbons" and are not separately determined.

Nitrogen.—Always estimated by difference.

In analysing a mixture of gases it is necessary to observe the correct order of using the reagents. *E.g.* in estimating oxygen in a mixture of nitrogen, oxygen and carbon dioxide, it is incorrect first to absorb the oxygen with alkaline pyrogallol, as this would also absorb the carbon dioxide.

Examples of Analyses with the Bunte burette.

1. **Air.**—Determine the percentage of oxygen by absorbing it with hyposulphite (best) or alkaline pyrogallol.

The percentage of carbon dioxide is too small to estimate accurately in 100 c.cs. Result should show about 20·5-20·6 % oxygen.

2. **Expired air from the lungs. Carbon dioxide, oxygen, nitrogen.**—Collect over water saturated with carbon dioxide. Absorb the gases in the above-named order. Replace the carbonic acid water with pure water after removal of the carbon dioxide.

3. **Flue gases. Carbon dioxide, oxygen, carbon monoxide, nitrogen.**—Collect over carbonic acid water. Absorb in above order, replacing the carbonic acid water with pure water after removal of the carbon dioxide.

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B. **The Hempel burette and pipettes.**—A simple form of Hempel's burette is shown in Fig. 61, which explains itself.

The burette holds as a rule exactly 100 c.cs. The gas may be confined over water or mercury, and is measured at atmospheric pressure by means of the levelling tube. To fill the burette, open *B* and connect *A* to *L* by

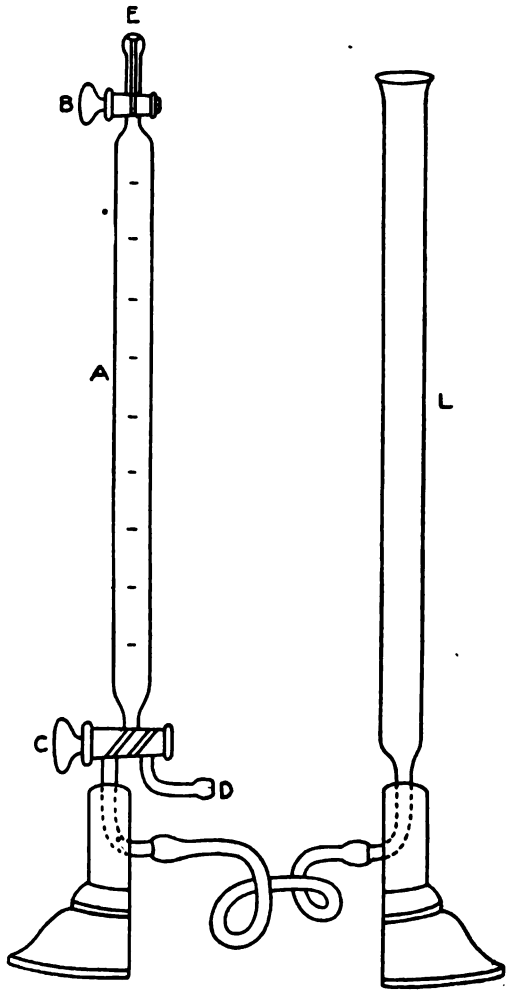

FIG. 61.

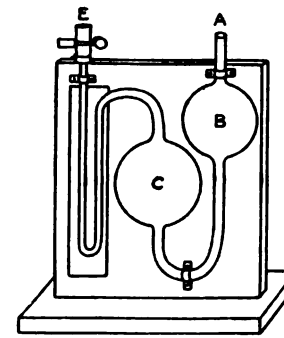

FIG. 62.

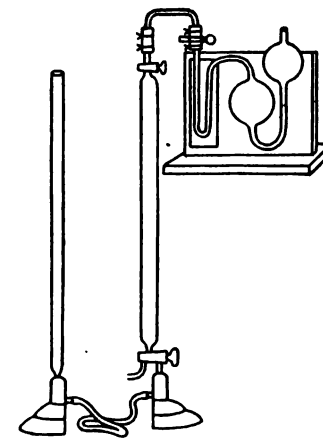

FIG. 63.

turning *B* to the necessary position. Pour water into *L* till it is about half full and raise *L* so as to fill *A* with water. Fill also the bore of the tap *B* and the capillary *E* with water, then connect *L* and *D* and likewise fill the bore of the tap and the capillary *D* with water.

To fill with gas, place *L* on the ground, connect *E* to the source of the gas, open *B* and connect *L* and *C*. Water runs from *A* to *L* and draws the

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gas after it. Bring to atmospheric pressure by raising *L* slowly till the bore of the tap *C* is just full of water. Close *C* and *B*. The burette now contains 100 c.cs. of gas at atmospheric pressure.

The reagents are each contained in a separate pipette. The simplest form is that shown in Fig. 62. The reagent is poured in at *A*, with clip at *E*

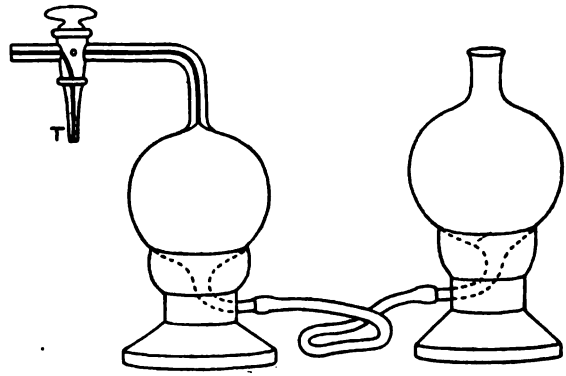

FIG. 64.

open. When bulb *C* is full the reagent is gently blown over into the capillary by blowing in at *A*, till it is full up to a mark near the rubber connection. Do *not* let the reagent touch the rubber. Bulb *B* should be empty.

All connections between burettes, pipettes, etc., must be made of stout rubber tubing, wired on. The necessary connections are usually made

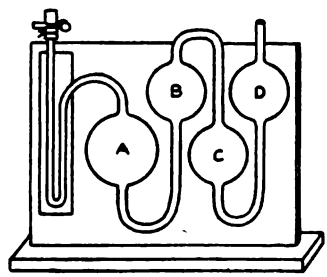

FIG. 65.

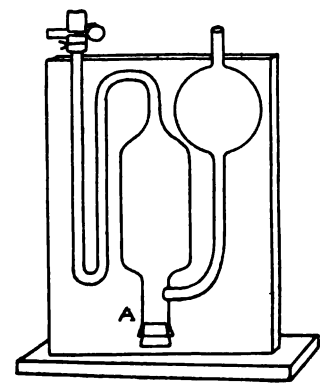

FIG. 66.

through stout glass capillary (thermometer) tubing. The ends of capillaries should meet inside the rubber connection.

The necessary connection between burette and pipette is made by means of a capillary bent twice at right angles. It should be filled with water before making the connection, and so also should the rubber tubing on the burette and pipette. The complete apparatus is shown in Fig. 63.

The gas is transferred from burette to pipette by raising *L*, opening tap *B*,

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and turning C to connect A and L. (Fig. 61.) Continue until water is just beginning to flow into the pipette. Close all taps. Shake the pipette (without disconnecting it) till absorption is complete, and draw the gas back into the burette by lowering L and opening the taps, till the reagent in the pipette again reaches the mark on the capillary.

Note.—In this way the capillary remains full of the gas. The error introduced is small and for ordinary purposes may be disregarded.

If the highest accuracy is desired, the Dreschmidt pipette may be used. In this the capillary is fitted with a three-way tap. (See Fig. 64.) The reagent is drawn up to this tap, *without allowing any to enter the bore*, and the tube T is then dipped into a basin of water (mercury, etc.) the tap turned to connect with the burette, and the gas in the connecting capillary drawn over into the burette with liquid from the basin.

Hempel's pipettes similarly fitted with a three-way tap can be obtained from most firms supplying gas apparatus.

A fresh pipette is of course necessary for each reagent.

Hempel's compound pipette, for containing reagents that are affected by the air, is shown in Fig. 65. The reagent is contained in A, B is empty, C is filled with reagent and D is empty. The liquid in C thus protects the main reagent from the air.

A pipette for solid reagents is shown in Fig. 66. The solid is introduced into the bulb through A, and the tubulus corked up securely. This pipette is used to contain sticks of phosphorus for oxygen determination. It is, of course, filled up with water in the usual manner after introducing the phosphorus.

It is also very advantageous to use this pipette for potash for carbon dioxide absorption. The large bulb is filled with little rolls of wire gauze or with broken glass, which when wet with potash offer a very large surface to the gas. Thus the absorption is complete in a few moments without shaking.

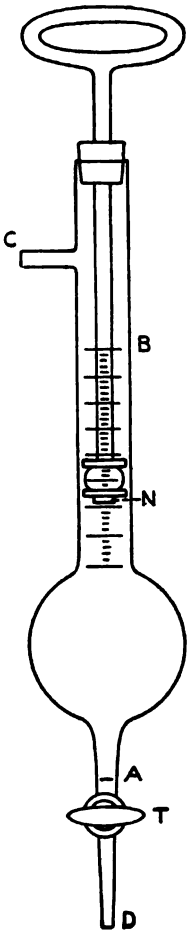

FIG. 67.

Note.—All shapes of Hempel's pipettes are obtainable fitted with stop-cocks, which are far preferable to the rubber connection and pinch-cock. Also the three-way tap above described should be obtained if possible, so that the Hempel pipette may be used in the same manner as the Dreschmidt pipette.

The warning not to allow reagents to enter the stop-cocks is here repeated.

C. **The Tollen's gas burette.**—This burette (Fig. 67) is very simple in construction and principle, depending on the use of a piston to draw in the absorbents. Its advantages are as follows:

(1) Rapid working.
(2) Simplicity.

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(3) No confining liquids required. Hence no error in the initial volume of gas due to absorption is introduced.

Its most serious drawback is that the percentages of gases to be absorbed must not exceed a certain obvious limit, viz. that of the lowest graduation on the stem.

To use the burette, oil the piston, which should work easily. (The fit may be adjusted by the nut *n*.) Fill with the gas to be analysed by drawing up the piston above the side-tube *c*, to which the rubber hand-bellows supplied with the instrument is attached. The iron tube for the flue or furnace from which the gas is to be taken is attached to jet *d*, and gas is drawn into the burette by working the bellows. Now close tap *t* and push the piston down till it just closes the side-tube *c*. Disconnect and transfer to water at constant temperature in a vessel of sufficient size to allow of the immersion of the burette to the zero mark *b*. Leave for some minutes. *In future the burette will only be touched* above *the zero mark for obvious reasons.*

To obtain 100 c.cs. of gas at atmospheric pressure, open tap *t* and hold burette so that the level of water *outside* is at mark *a*. Push down the piston till the lower edge of the nut *n* is at zero mark *b*. Close tap.

Dip *d* into a basin containing some of the necessary reagent (these to be employed in the correct order as already indicated) and draw a few c.cs. into the burette by opening *t* and raising the piston. When absorption is complete, expel the reagent and draw in water with which the burette is rinsed. Repeat two or three times, finally expel the water to the mark *a* so that the pressure is atmospheric, as before.

Note.—The student should now be in a position to understand, without further description, other makes of absorption apparatus, such as **Orsat's, Allen's, Winkler's,** etc. It may be stated that most of these are for the purpose of flue and furnace gas analysis, and are supplied in a readily portable form.

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CHAPTER II.

COMBUSTION METHODS.

In analysing such things as coal-gas, the non-absorbable residue will contain hydrogen and methane. These are most easily determined by first burning the hydrogen and then the methane. This fractional combustion is carried out by passing the gases, mixed with air, through a capillary tube (Fig. 68) containing a small roll of palladiumised asbestos. (These tubes may be purchased from the usual sources.)

Fig. 68.

To carry out an analysis, the non-absorbable residue consisting of hydrogen, methane and nitrogen is mixed with excess of air. This is carried out as follows. Usually far too much gas will be left in the burette to allow of excess of air entering, so after measurement of its volume all the gas except about 20-25 c.cs. is driven out of the burette by raising the levelling tube and connecting the burette with the open air through *E*. (Fig. 61.) The volume remaining is now measured at atmospheric pressure in the usual way. By now lowering *L* and again connecting the burette with the air, about 70-75 c.cs. of air are drawn in, the tap *B* closed, and the volume again measured at atmospheric pressure. The volume of air drawn in is thus measured.

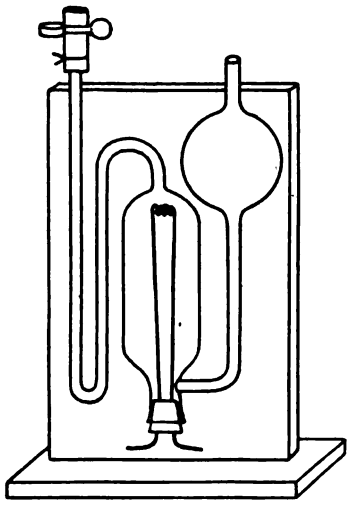

Fig. 69.

Now connect the burette to a pipette containing water by means of the palladium capillary. Heat the palladium to 400° C. (a spirit-lamp is just right) and when hot pass the gas very slowly from burette to pipette and back again, *on no account allowing water to enter the capillary*. Repeat once more. Measure the contraction. From the equation

$$2H_2 + O_2 = 2H_2O$$

we see that $\frac{2}{3}$ of this contraction is due to disappearance of hydrogen. Calculate from this the volume of hydrogen in the *total original volume of non-absorbable residue.*

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The methane is now determined by disconnecting the palladium capillary and connecting the burette to a Winkler combustion pipette (Fig. 69). This is simply a Hempel pipette for solids, fitted with two leads joined inside the bulb by a spiral of platinum wire. The large bulb and capillary are filled with water.

Connect the terminals to a battery of sufficient voltage to heat the platinum coil to redness. Switch on the current *first* * and *then* pass the gas slowly over into the pipette. As soon as the water leaves the platinum wire the latter glows and combustion starts. Pass the gas in gradually till it is all transferred to the pipette. Switch off the current and leave some time for the gas to cool. Draw the gas again into the burette and without measuring the contraction pass it over into a potash pipette to absorb the carbon dioxide. Now transfer to the burette and measure the total contraction. From the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$ it is seen that, as the substances on the right-hand side have been removed, $\frac{1}{3}$ of the total contraction is methane. Hence calculate the volume of methane in the whole of the non-absorbable residue. The nitrogen in the non-absorbable residue is now obtained by difference.

Examples of analyses by the Hempel burette and combustion apparatus.

1. Water gas :—carbon dioxide, oxygen, carbon monoxide, hydrogen and nitrogen.—Absorb the first three constituents in the order named. Determine

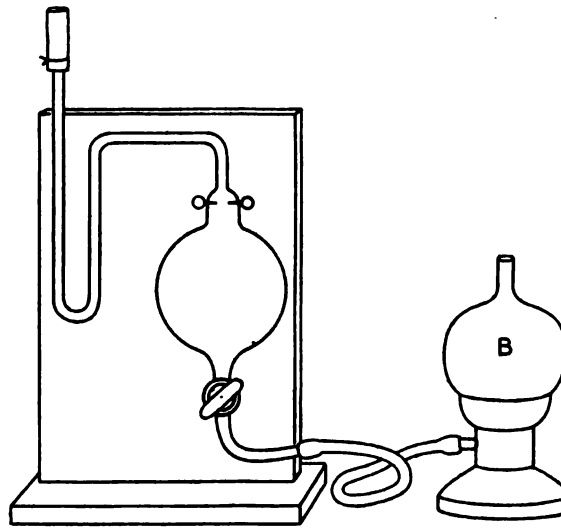

FIG. 70.

the hydrogen in a portion of the residue mixed with air by the palladium capillary or by an *explosion pipette*, shown in Fig. 70. This contains *mercury*, and is furnished with two platinum wires connected to terminals outside, by

* Otherwise an explosion will shatter the pipette.

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which the gas in the bulb may be exploded by connecting the terminals to those of a Ruhmkorf coil.

Before drawing the gas into the pipette, the capillary and connecting tube are filled with mercury by raising the reservoir *B*. The gas is *drawn* into the pipette by lowering the reservoir *B* and raising the levelling tube, as it is not possible to push the gas in from the burette with a levelling tube containing *water*. The gas is exploded, allowed to cool and pushed back into the burette, and the contraction measured. Hence follows the volume of hydrogen in the whole non-absorbable residue, and the nitrogen by difference.

2. **Analysis of coal-gas.**—Coal-gas as supplied contains carbon dioxide, "heavy hydrocarbons," oxygen, carbon monoxide, hydrogen, methane, nitrogen.

The gas must be confined over water saturated with coal-gas, as most of the constituents are appreciably soluble. (Shake water thoroughly with gas in a Winchester bottle.) 100 c.cs. of the gas are then measured in the Hempel burette.

The reagents are used in the following order: Potash, bromine water, hyposulphite, ammonia-cuprous chloride (twice), and then a measured fraction of the residue mixed with air and the hydrogen determined by the palladium capillary and the methane by the Winkler pipette.

If it is desired to know the ethylene and benzene vapour contents separately, the method recommended by Haber is used.

The absorption of ethylene by bromine water depends on the formation of ethylene dibromide, $C_2H_4Br_2$, whilst the absorption of benzene is merely a solution.

The Bunte burette is the most convenient for this, as the bromine water is readily washed out of it, as already described. The diminution in volume is measured by allowing a solution of potassium iodide (not water) to enter the burette after shaking with the bromine water.

The diminution in volume = the total "heavy hydrocarbons." The iodine liberated is titrated with thiosulphate. The bromine water is also titrated with thiosulphate, after adding to potassium iodide solution a volume equal to that employed for the coal-gas. The difference gives the weight of bromine used by the ethylene.

Since $C_2H_4 = Br_2 = I_2 = 2Na_2S_2O_3$,

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = \cdot 001402 \text{ gm. ethylene.}$$

This weight = 3·45 c.cs. of *dry* ethylene at N.T.P.

The volume when moist and at observed temperature and pressure is readily calculated.

This volume, subtracted from the total volume of "heavy hydrocarbons," gives the volume of benzene vapour.

3. **Producer gas, semi-water gas or Dowson gas, Mond gas, etc., are similarly analysed.**

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CHAPTER III.

DETERMINATIONS BY GASOMETRIC METHODS.

ANY reaction in which a gas is quantitatively evolved may be used to determine the substance evolving the gas.

Lunge's nitrometer or gas-volumeter may be used for the reactions.

The nitrometer has already been described. It is used for the estimation of nitric acid and nitrates (see p. 219).

By the same reaction the nitro-group in nitro-glycerine, nitro-cellulose, etc., may be determined, the substance being first dissolved in strong sulphuric acid and the estimation carried out exactly as described on page 220.

For other reactions evolving gases that are used to estimate the reacting substances, the gas-volumeter is employed. This may be the nitrometer itself, with the addition of a small reaction flask which is connected to the exit tube at the top of the nitrometer by rubber tubing. In the usual form of gas-volumeter the funnel with which the nitrometer is supplied is omitted, but it is not necessary to have a separate apparatus, though of course more convenient.

Moreover, Lunge has improved the gas-volumeter by the addition of a compensation tube by which the volume of the gas evolved in the reaction is automatically reduced to N.T.P. This again is merely a time-saving device for technical work.

Both forms of apparatus will now be described. The simple form is shown in Fig. 71.

The reaction flask is made with two compartments to keep the reagents separate until the apparatus is fitted up. The substance to be estimated is weighed into the outer compartment and the reagent is placed in the inner one. The confining liquid in the volumeter is usually mercury. The actual estimation is carried out as follows.

The flask containing the substance and reagent, immersed in a water-bath, is attached to the measuring tube as shown, and the glass tap is removed. The mercury in the vessel is adjusted to zero by raising or lowering the levelling tube, and the tap is replaced in the closed position.* Lower the levelling tube somewhat to avoid pressure in the apparatus, and turn the tap to connect

* If the ordinary form of nitrometer is used, the pressure in the flask is made equal to atmospheric pressure by raising or lowering the levelling tube with the tap removed as before. The tap is then replaced so as to connect the measuring tube with the funnel, and the air in the measuring tube is driven out by raising the levelling tube. Close the tap. The apparatus is now ready for the experiment.

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the reaction flask to the measuring tube. Gently tilt the flask so that a *little* of the reagent comes into contact with the substance. Do not pour it all in at once. Continue until the reaction is over. Lower the levelling tube as may be necessary to avoid pressure. Allow the flask to cool in the water-bath for at least 5 minutes. Then adjust the pressure to atmospheric, read the volume of the gas, and the barometer and thermometer. The calculation is then carried out in a similar manner to that shown on page 220.

In the improved form (Fig. 72) the reduction tube is worked as follows:

The volume of air in the reduction tube is so compressed by raising the levelling tube that it occupies the volume it would occupy at N.T.P. Since

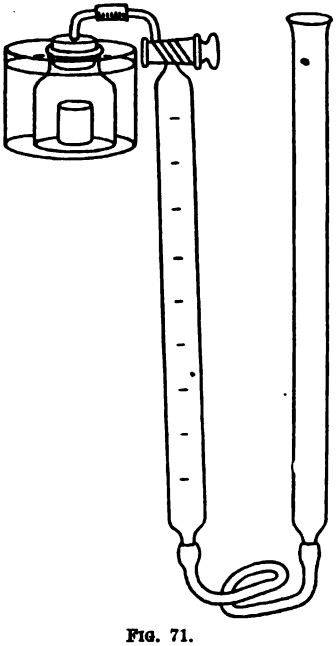

FIG. 71.

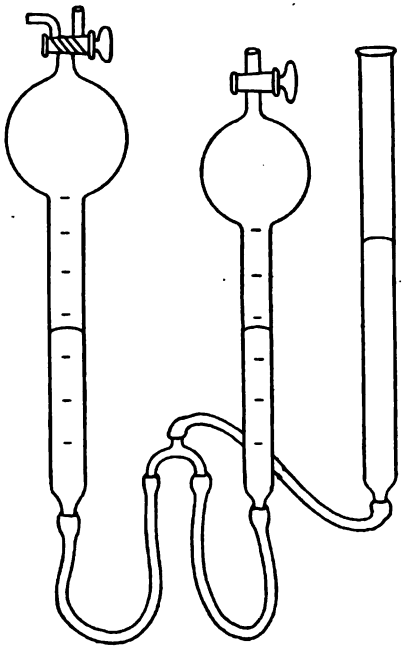

FIG. 72.

this pressure is transmitted to the gas in the measuring tube, this also will occupy the volume it would occupy at N.T.P.

The working will be best illustrated by an example. Suppose the temperature and pressure at the time of the experiment are 15° C. and 750 mm. The pressure of aqueous vapour at 15° C. being 12·7 mm., the volume of *moist* air which will occupy 100 c.cs. at N.T.P. is given by

$$V_{15 \cdot 750 \cdot 12 \cdot 7} = \frac{100(273+15)760}{273(750-12 \cdot 7)} \text{ c.cs.}$$

$$= 105 \cdot 1 \text{ ccs.}$$

This volume of air is then drawn into the reduction tube by lowering the levelling tube. The adjustment is made by making the levels of mercury in the two tubes the same. A drop of water is then added to the reduction

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tube and the tap closed. If the gas is to be measured dry, the correction for aqueous vapour tension is omitted from the calculation, and a drop of strong sulphuric acid is added to the air in the reduction tube.

The experiment is now carried out as before, first making the pressure in the reaction flask and measuring tube the same as atmospheric pressure just as already described. The final volume of the evolved gas is read thus:

(1) Raise the levelling tube so that the volume of gas in the reduction tube is exactly 100 c.cs. Clamp it.

(2) By means of the special double clamp raise or lower the reduction and levelling tubes simultaneously till the level of mercury in the measuring tube is the same as that in the reduction tube, as shown in the figure. The volume of gas is now exactly what it would be at N.T.P.

Note.—In all determinations, a weight of substance to be determined must be taken such that the volume of gas evolved will be somewhat less than the capacity of the instrument. This is usually 50 c.cs. or 100 c.cs.

By means of the gas-volumeter the following determinations may be carried out:

1. **Determination of the equivalent weight of any metal that evolves hydrogen from hydrochloric acid.**—A suitable quantity of the pure metal is weighed and put into the outer compartment of the reaction flask. Hydrochloric acid of the necessary strength is placed in the inner compartment.

Calculate the weight of metal that liberates 1 gm. (11·126 litres) of *dry* hydrogen at N.T.P.

2. **Determination of carbonates by the volume of carbon dioxide evolved.**—The ordinary form of gas-volumeter is used. The carbonate is placed in the outer compartment, and dilute sulphuric, hydrochloric or nitric acid, saturated with carbon dioxide by adding a pinch of sodium bicarbonate, in the inner compartment of the reaction flask. The volumeter contains water saturated with carbon dioxide. Reduce the volume of gas obtained to N.T.P. (*dry*). The density of dry carbon dioxide at N.T.P. = 1·5225 gms. per litre.

3. **Valuation of pyrolusite.**—About 0·2 gm. of very finely-powdered pyrolusite is placed in the outer compartment of the reaction bottle and 5 c.cs. of 4N. sulphuric acid added to it. Leave for 5 minutes. Put 25 c.cs. of "10 volume" hydrogen peroxide in the inner vessel. Attach to the volumeter and carry on as usual.

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2.$$

Density of dry oxygen at N.T.P. = 1·42923 gms. per litre.

From the equation we see that 32 gms. oxygen = 86·93 gms. MnO_2.

4. **Determination of hydrogen peroxide or of potassium permanganate.**

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Hence $$O_2 = \frac{2KMnO_4}{5} = H_2O_2.$$

If peroxide is being determined place it in the outer compartment of the reaction flask and sulphuric acid and permanganate solution in the inner one. The liquid must still contain permanganate when the reaction is over.

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If permanganate is being determined, the solution is placed in the outer compartment, a suitable amount of sulphuric acid added, and the hydrogen peroxide is placed in the inner compartment. At the end of the reaction the liquid must contain *no* permanganate. Calculate as in 3.

5. **Determination of urea.**—The urea is oxidised by a strongly alkaline solution of sodium hypobromite.

$$CO(NH_2)_2 + 3NaOBr = CO_2^* + N_2 + 3NaBr + 2H_2O.$$

Density of dry nitrogen at N.T.P. = 1·2505 gms. per litre.

6. **Determination of ammonia** (Knop and Wagner).—The ammonia is oxidised by hypobromite as in 5.

$$2NH_3 + 3NaOBr = N_2 + 3H_2O + 3NaBr.$$

Owing to the fact that this reaction is not quite quantitative at ordinary temperatures, the result is compared with the volume of nitrogen obtained from a solution of ammonium chloride of accurately known strength.

Literature.

Handbook of Volumetric Analysis. SUTTON. (Churchill.)
Quantitative Inorganic Analysis. MELLOR. (Griffin.)
Standard Methods of Chemical Analysis. SCOTT. (van Nostrand.)
Quantitative Analysis. TREADWELL. (Hall). (Wiley.)
Select Methods of Chemical Analysis. CROOKES. (Longmans.)
† Agricultural Analysis. ADDYMAN. (Longmans.)
Quantitative Analysis by Electrolysis. CLASSEN. (Wiley & Sons.)
Practical Methods of Electro-Chemistry. F. M. PERKIN. (Longmans.)
Gas Analysis. HEMPEL. (Macmillan.)
Gas Analysis. FRANZEN. (Blackie.)
Complete course of Volumetric Analysis. BOONE. (Blackie.)
Quantitative Analysis. CLOWES & COLEMAN. (Churchill.)

* Absorbed by the alkali. † Introduction to Commercial Analysis.

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BOOK IV.

ORGANIC PREPARATIONS.

PART I.

INTRODUCTION.

GENERAL HINTS IN PRACTICAL ORGANIC WORK.

WHEN about to do an experiment, carefully read through the method first, noting all necessary apparatus and precautions. In the qualitative work, do the operations in a quantitative manner, weighing or measuring all substances used and endeavour to obtain the maximum yield. A rough balance is necessary.

It is needless to dilate upon the need for absolute cleanliness. When uncertain as to the manner in which an experiment will proceed, make a preliminary trial in test-tubes: use these also for tests given at the end of preparations.

In preliminary trials connected with crystallisation, it is a good plan to place a little of the liquid which is expected to deposit crystals in a watch-glass and cool. An indication of the yield will thus be given.

Whenever an inflammable liquid is used (ether, carbon disulphide, etc.), great care must be taken to avoid risk of fire. Do not have naked flames near, and when evaporating such liquids always use a bath of hot water *without* a flame under it, if the boiling-point permits (as it generally does).

Do not use vessels much too large or small for an experiment: connect apparatus neatly, avoiding unnecessary lengths of rubber tubing, etc.

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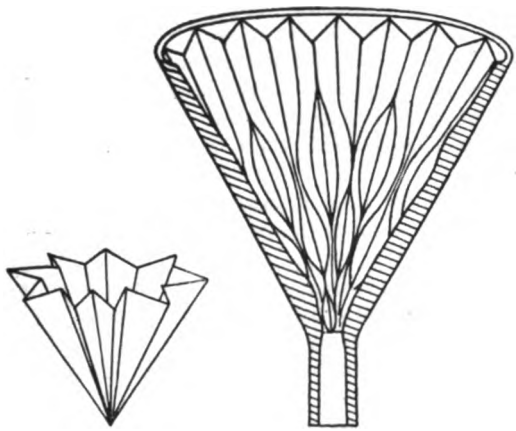
CHAPTER I.

GENERAL OPERATIONS.

A. **Filtration.**—Whereas in inorganic preparations the use of the filter-pump is frequent, it is there described; here a few other devices by which filtration can be accelerated are noted. (See also pp. 1 and 2.)

A folded filter may be used, as in Fig. 73*a*, or a ribbed funnel as in Fig. 73*b*. The filter-pump is used in connection with a glass-funnel fitted with a porcelain plate or a porcelain funnel, of which the perforated plate is a part. The



(*a*) FIG. 73. (*b*)

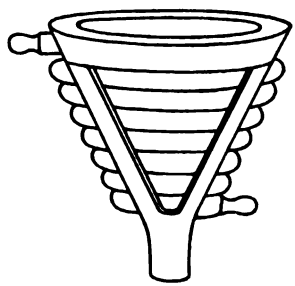


FIG. 74.

objection to the last-named is the difficulty of cleaning it thoroughly. In either case the filter-paper is first moistened with the liquid present in the mixture, the paper carefully laid over the perforated plate (it should be only very slightly larger than the plate), and gentle suction applied. (For filter-pump see p. 1).

In some cases it is necessary to keep the solution hot whilst filtering, *e.g.* draining crystals from a saturated solution. This is done by surrounding the funnel with a hot-water jacket or a coil through which steam is passed (Fig. 74). (See also Fig. 2, p. 2.)

B. **Crystallisation.**—When preparing solid substances, they are obtained, if possible, as well-defined, fair-sized crystals. When crude substances are dissolved in a solvent and crystallised, the impurities remain in the mother-liquor, hence crystallisation is the chief means of purifying substances.

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Choice of the solvent.—Preliminary experiments should be done with small quantities of the substance in various solvents, and the suitability of each noted. The solvents in general use are:

Water.	Alcohol.	Ether.	Petrol.
Benzene.	Glacial acetic acid.	Acetone.	Chloroform.
Carbon disulphide.	Aniline.	Toluene.	Xylene, etc.

Sometimes mixtures of these are used, *e.g.*:

Water and alcohol. Alcohol and ether. Benzene and petrol.

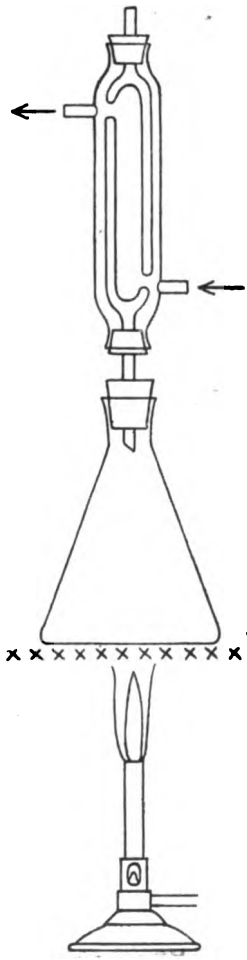

FIG. 75.

The most suitable solvent is that which dissolves the substance with difficulty when cold but readily when hot.

Sometimes the most convenient method is to dissolve the substance in a solvent which dissolves it readily, and to add to the solution a liquid in which it is not readily soluble.

Preparation of the solution.—To the well-powdered substance a small quantity of the solvent is added and the mixture warmed. This is done in a basin or beaker unless the solvent is very volatile, heating on a wire gauze. More solvent is gradually added till the solid is *just* dissolved. Avoid using more solvent than necessary; if a small residue is left which will not dissolve, it is probably some impurity and should be filtered off.

If a volatile or inflammable solvent is used, the solution should be made in a flask fitted with a reflux condenser, as in Fig. 75.

N.B.—This apparatus is in frequent use for boiling volatile things together for any length of time. The condensed vapours return to the flask.

The solution should always be filtered unless it is perfectly clear.

1. *Production of the crystals.*—By cooling the hot saturated solution. This is done when the solvent dissolves the substance sparingly when cold, readily when hot.

It may occasionally be necessary to cool the solution below the ordinary temperature in a freezing mixture, but in any case very small crystals should be obtained (by rapid cooling and shaking or stirring), as large crystals are liable to enclose some of the mother-liquor.

If crystallisation is slow, add a crystal of the substance to the solution and stir well. This is called "seeding," and sometimes brings down an immediate and copious crop of crystals.

If the solution is too strong, the substance will sometimes come out as

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an oil because deposition begins above its melting-point. In this case, the solution must be warmed and a little more solvent added.

2. *Crystallisation by evaporation.*—If no solvents give solutions which vary greatly in concentration at different temperatures, the substance is crystallised from solution after filtration, by slowly evaporating the liquid in a shallow open dish. To prevent dust getting into the liquid, the dish is covered with a large funnel.

The solvent must not be allowed to evaporate completely, or the impurities will be mixed with the crystals. Crusts deposited on the sides of the vessel should not be mixed with the crystals, but worked up again with the mother-liquor.

The evaporation is a lengthy process, but may be sometimes hastened by inclining the vessel so that the vapour, which is almost always heavier than air, may pass away more quickly; or a gentle current of filtered air may be passed over the surface. Again, the vessel may be placed in a desiccator containing some suitable absorbent for the solvent (*e.g.* sulphuric acid for water, paraffin wax for ether), and the desiccator may then be exhausted by a filter-pump. (Vacuum desiccator, Fig. 76.)

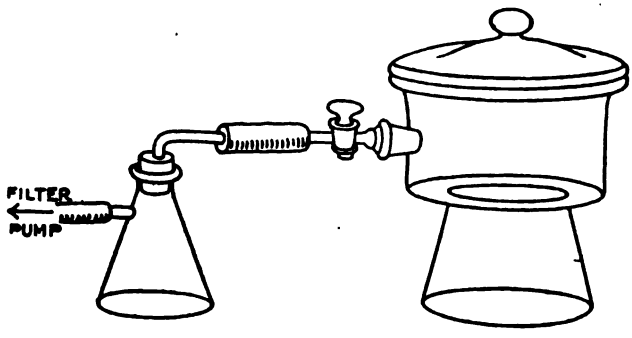

FIG. 76.

3. *Crystallisation by the addition of a second liquid.*—If it be found that a substance is soluble in one liquid but not in another (the two liquids being completely miscible), a solution in the one liquid is made, and the other is added to it till a turbidity appears. This often contains impurities and should be filtered off through a heated funnel. The filtrate is then set to crystallise in a crystallising dish.

Collection and purification of the crystals.—The crystals are filtered (first removing any crusts), washed on the filter with *small* quantities of the solvent, and if the solvent is one of high boiling-point it is gradually displaced by a more volatile one such as ether or petrol, using first mixtures of the two liquids, finally the more volatile one alone.

The mother-liquors will yield a further crop of crystals on further evaporation, etc., if the body is fairly soluble, but these must usually be purified by fractional crystallisation. (See p. 3.)

Sublimation.—Some substances (*e.g.* naphthalene, camphor, benzoic acid, etc.) sublime readily, and their vapours may be condensed on a cold surface

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in a crystalline form. The impure substance may be placed in a basin over which a funnel is placed. On warming the basin the body sublimes on to the funnel. Brühl's apparatus for this purpose is shown in Fig. 77*a*; another in Fig. 77*b*.

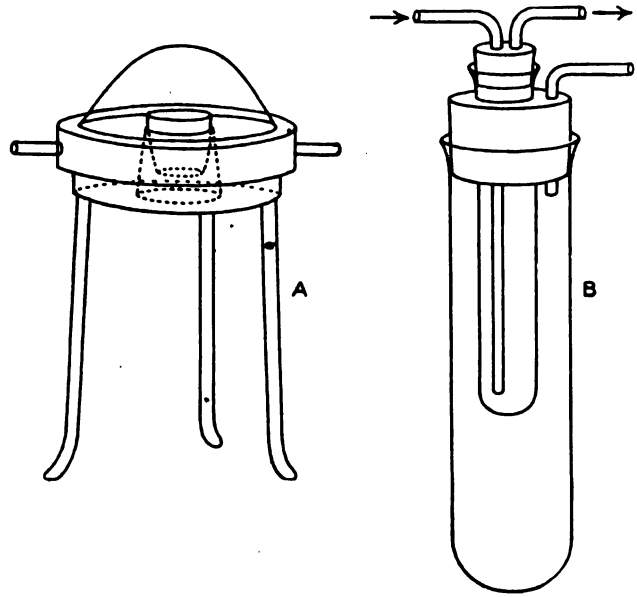

FIG. 77.

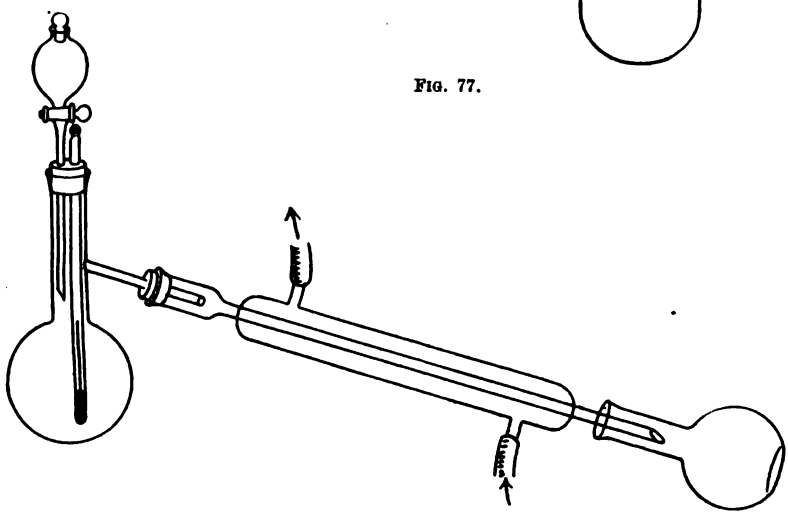

FIG. 78.

C. **Distillation.**—1. For most purposes the apparatus consists of a distilling flask with side tube, a condenser (water- or air-cooled), and a receiver.

The flask should be round-bottomed, closed with a cork or rubber stopper, carrying a thermometer. For liquids boiling below 80° C. a water-bath is used. On no account should anything else ever be used for an inflammable liquid, in which case it is safest to heat the water *before* immersing the flask.

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If it is necessary to apply heat to the water whilst the distillation is proceeding, some form of screen to prevent vapour reaching the flame will be necessary. Another method is shown in Fig. 81.

Liebig's condenser is shown in Fig. 78. The double surface form is more compact. (Fig. 75.)

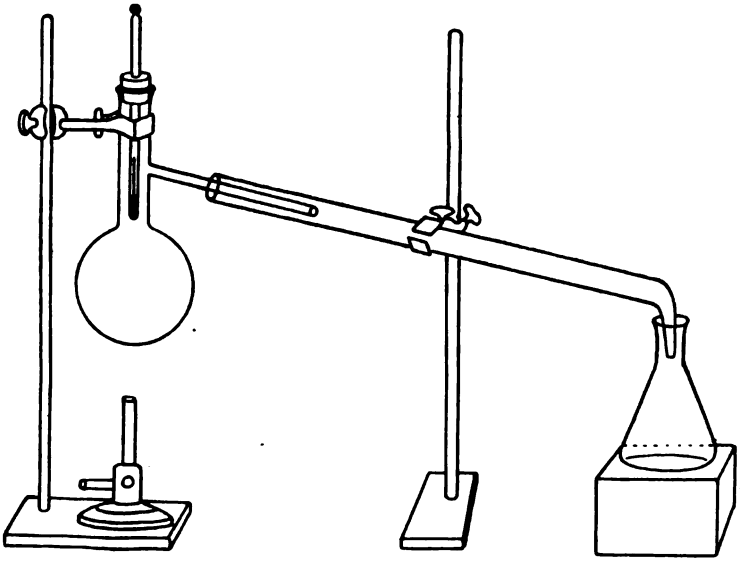

FIG. 79.

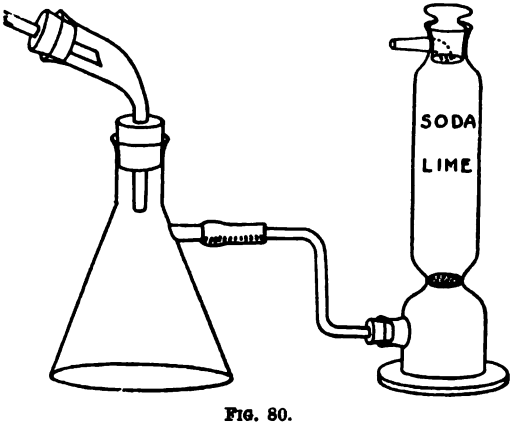

FIG. 80.

If the B.P. of the liquid is above 100° C., a water condenser should not be used, but a plain long tube, air-cooled. (Fig. 79.) If the substance tends to solidify in the condenser it should be as wide as possible.

The receiver may, for most substances, be placed over the end of the condenser, but in the case of volatile or inflammable liquids it is necessary

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to fit an adapter as in Fig. 80. It is sometimes useful to have the adapter dipping under ice-cold water.

For liquids easily acted on by the moisture of the air (*e.g.* the acyl chlorides, etc.), the receiver must have a side-tube, which is attached to a vessel containing a drying agent. (Fig. 80.)

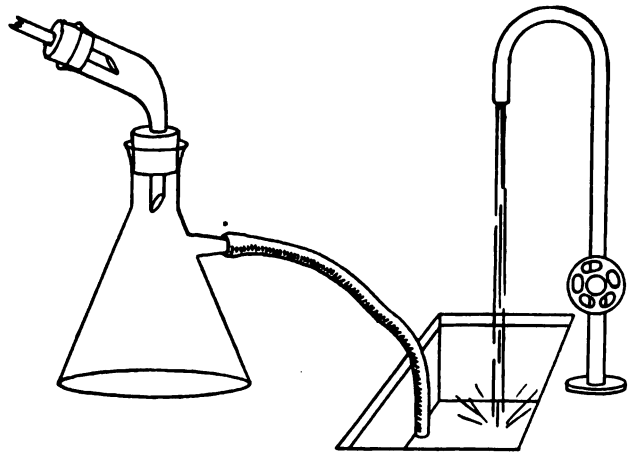

FIG. 81.

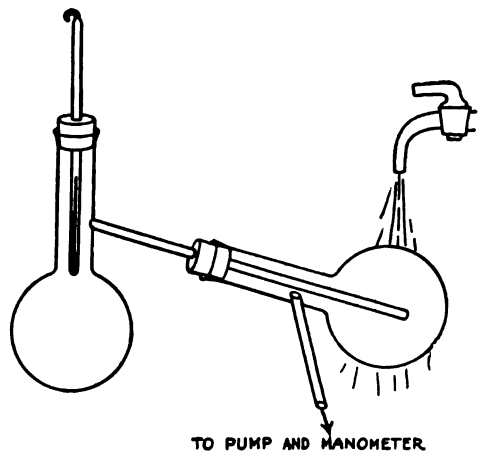

FIG. 82.

When a small test portion of a liquid is being distilled the condenser may be omitted and the receiver cooled by a stream of water from the tap. (Fig. 82.)

In case of very volatile liquids it is often necessary to immerse the receiver in ice.

2. *Fractional distillation.*—When two or more miscible liquids whose boiling-points are not too close together are to be separated, the mixture is distilled and fractions are collected, the receiver being changed every 10°

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rise in temperature. These fractions are then placed one at a time into a smaller flask and distilled to dryness, fractions from each portion being collected in the receivers which have already been used, and labelled with the required temperatures. If necessary the process can be repeated, changing the receiver every 5° rise. It will be found that the mixture is thus separated into two main fractions, one boiling near the B.P. of the lower-boiling liquid and the other near that of the higher. The intermediate fractions are small and get smaller as the fractionation proceeds.

It often happens that the boiling-point of the mixture does not rise steadily from the lower to the higher B.P., but that a mixture having a constant

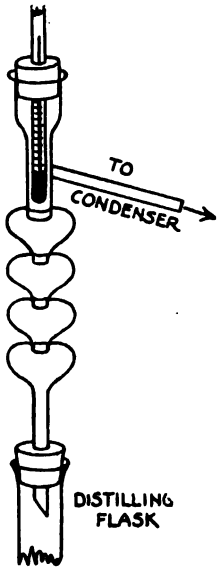

FIG. 83.

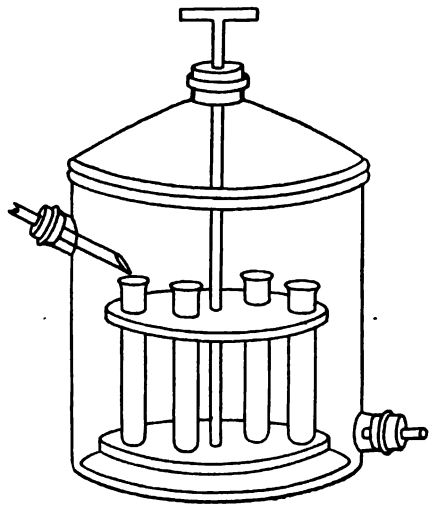

FIG. 84.

B.P. is obtained. In this case other means must be sought to effect the separation.

Though not absolutely necessary, fractionation is effected more easily and completely by the aid of a Young's fractionating column, of which various forms exist. One is shown in Fig. 83. One careful distillation with a column will give the same effect as several without it.

3. *Distillation under reduced pressure.*—Substances often decompose if heated to boiling under atmospheric pressure. In these cases it is necessary to distil under reduced pressure. The apparatus is made air-tight by the use of rubber stoppers and the receiver is attached to a suction flask which is exhausted by a filter-pump with a manometer. (Fig. 82.)

Liquids boiling under reduced pressure are apt to "bump." This is minimised by placing small pieces of unglazed porcelain, glass capillary tubes, etc., in the distilling flask, or by drawing a gentle current of air through a capillary tube passing through the cork and dipping into the boiling liquid.

4. *Fractional distillation under reduced pressure.*—The difficulty here is in

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collecting the separate fractions without having to stop the process. Many devices are in use to avoid this, *e.g.* Brühl's receiver, Fig. 84; Raikow's, Fig. 85.

The chief drawback to this and similar devices is that the liquid condenses to some extent in all the vessels. This is overcome by the arrangement in Fig. 86. The three taps are arranged so that the apparatus may be kept at the diminished pressure whilst the receiver is changed. Tap *C* is a three-way tap. When about to change the receiver, close tap *A*, open *B* and turn *C* so that it allows air to enter the flask only. The liquid meanwhile condenses in the bulb, and when the fresh receiver is attached, *C* is turned so that it connects the receiver to the pump. After a time *B* is closed and *A* opened, when the distillate collects in the receiver.

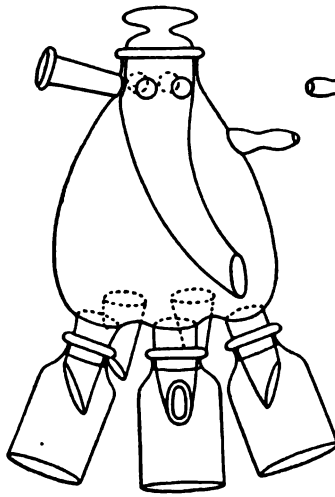

FIG. 85.

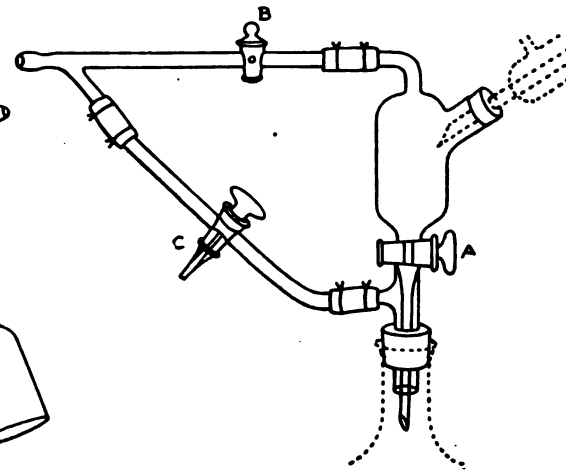

FIG. 86.

5. *Distillation with steam.*—Several bodies of high B.P. have an appreciable vapour pressure at 100°; hence a convenient way to separate them from the reaction mixtures is to blow steam through the boiling liquid. The substance volatile with steam comes over with the water, and the process is continued till nothing but water is seen in the condenser. (If the substance is soluble in water, *e.g.* acetic acid, a test for it is applied to a portion of the distillate until the body can no longer be detected.)

The apparatus consists of a steam generator (a large tin can), half filled with water and fitted with a long tube as safety valve, and a delivery tube leading to the distillation flask. This tube is of the shape shown in Fig. 87, and reaches to the bottom of the flask, which is tilted as shown to prevent spray entering the condenser. The rest of the apparatus will readily be understood from the figure. The flask should not be more than half full, and is also heated.

D. **Separation of liquid mixtures and solutions.** (See "Partition Coefficients" in the Physical Chemistry section.)—Many organic bodies can be

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separated from aqueous solution by shaking with a liquid non-miscible with water. Ether is most often used, though sometimes petrol, benzene, carbon disulphide or chloroform are also employed.

The extraction is made by shaking the cold solution with ether, etc., in a separating funnel (Fig. 88). The minimum of the extraction liquid should be used. The ethereal, etc., solution is drawn off, dried by calcium chloride or other desiccating agent, and the ether, etc., distilled off.

Sometimes, if the partition coefficient of the substance for ether-water is small, several successive portions of ether must be used.

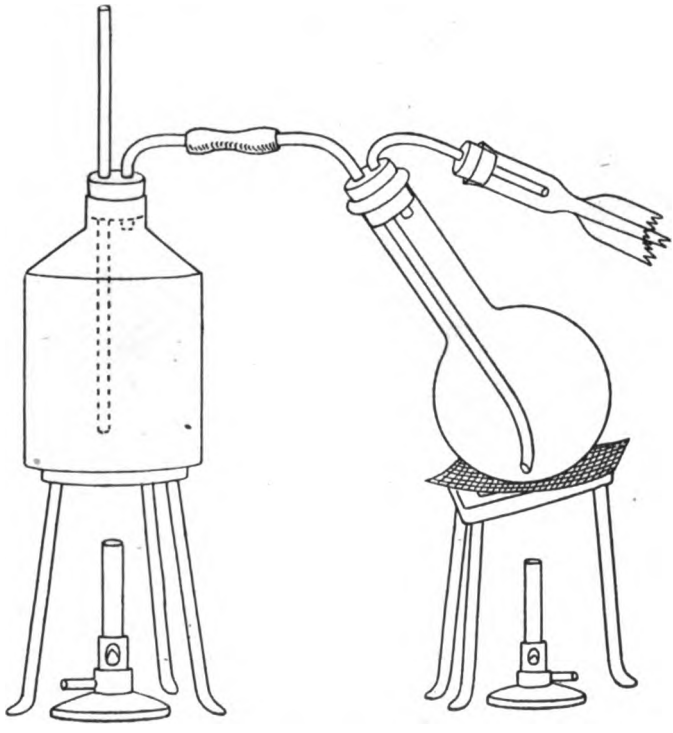

FIG. 87.

Fig. 89 shows an apparatus for the separation of *small* amounts of liquids.

If a large volume of solution is to be extracted, salt should be added to the aqueous solution as ether is soluble to the extent of 8-9 % in water but not in brine. Even if salt throws the substance out of solution it does not matter.

Ethereal extraction is also useful for isolating substances which emulsify with water, *e.g.* phenyl hydrazine.

E. **Salting out.**—In many cases, bodies which dissolve readily in water do not dissolve easily in salt solution, so that if salt is added to the aqueous solution they will separate; *e.g.* salt added to a soap solution causes the

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precipitation of the soap. The salts most commonly used are sodium chloride and potassium carbonate.

F. **Extraction of a solid from a mixture.**—This is carried out by digesting the mixture with a suitable solvent in which all but the desired substance are insoluble. The digestion is carried out by means of Soxhlet's apparatus, Fig. 90.

The mixture is introduced into the tube (A) in a cartridge of pure filter-paper. (These are sold for the purpose.)

The solvent is placed in the flask, which is of such a size as to hold, when not more than half-full, rather more of the solvent than the tube (A). The

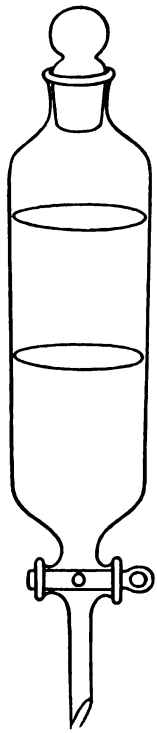

FIG. 88.

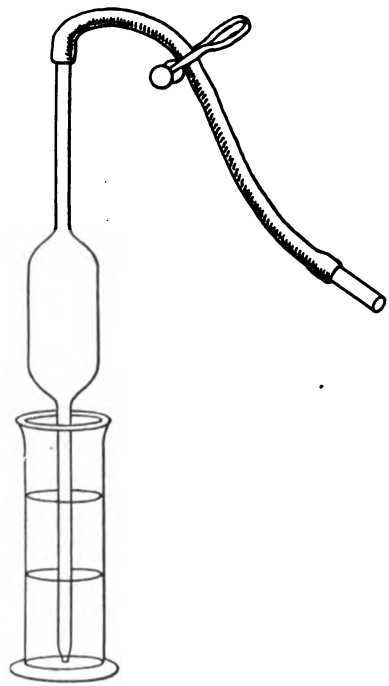

FIG. 89.

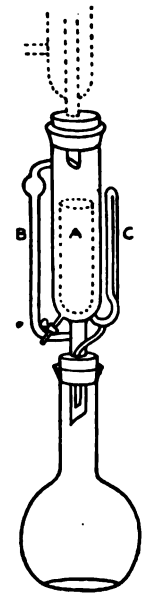

FIG. 90.

apparatus is put up as shown and the solvent boiled. The vapour goes *via* (B) to the reflux, from which it drops into the substance. When (A) is full up to the top of the syphon (C) the solution syphons back into the flask and the process is repeated automatically as often as desired.

Many examples in the use of this will appear in the following pages. It is also used for the determination of fat in various substances, such as feeding-stuffs. In this case ether is the solvent. When the extraction is complete it is evaporated and the remaining solid weighed.

A useful addition to the apparatus is a small tap at the bottom of (A), by which a test portion of the extract may be removed from time to time in order to see when the extraction is complete.

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CHAPTER II.

DETERMINATION OF PHYSICAL CONSTANTS.

In order to test the purity of an organic body and also as a means of identifying many substances, it is necessary to find the melting or boiling-point.

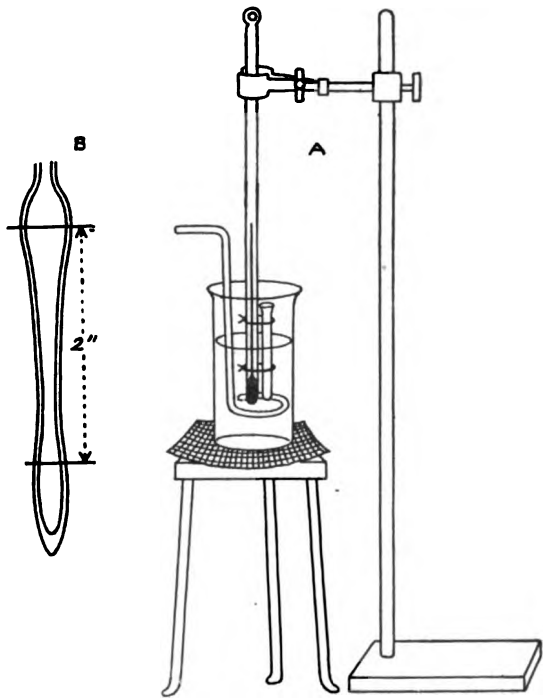

Fig. 91.

A. **Melting-point.**—Every pure body has an exact melting-point; if a substance gradually gets soft when heated and melts by degrees, it is impure.

Anomalous results are sometimes met with, *e.g.*:

One substance has two melting-points. This is due to the presence of two forms, each with its own melting-point.

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Mixtures often possess a melting-point lower than that of either constituent, with minima for particular proportions, indicating the formation of a compound.

There are several methods of finding the melting-point.

I. Take a small beaker, put some water in it (if the melting-point is below 100°, which can readily be seen by dipping a test-tube containing a small amount of the body into boiling water), or glycerine, sulphuric acid or potassium sulphate in sulphuric acid if the melting-point is below 240°, 290°, or 350° respectively. Draw out a piece of test-tube into the capillary shape shown in Fig. 91, and cut it so that one end is wide and the other narrow. Close the narrow end by holding in a flame for a moment. Put a *very small* quantity of the substance into this tube and shake it to the bottom. If too much is used the liquid may rise in temperature several degrees whilst the substance is melting. Attach the capillary to the bulb of a thermometer by a small rubber ring or platinum wire, and warm the liquid, quickly at first, then very slowly, with constant stirring, as the melting-point is approached. At the first sign of melting take the temperature.

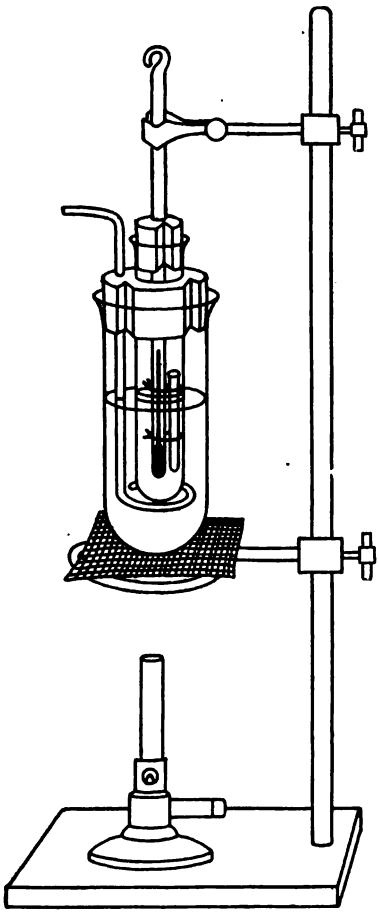

FIG. 92.

The thermometer must be accurately calibrated, and if an appreciable portion of the thread is exposed the following correction should be applied:

True temperature $= T + 0{\cdot}000154n(T - t)$,
where T is the apparent temperature,
t is the mean temperature of the exposed thread.
n is the number of degrees on the exposed stem.

II. A more convenient apparatus is shown in Fig. 92, which permits of more even heating. Several other forms have been devised which allow the stem of the thermometer to be immersed in the liquid bath.

As examples use *o*-nitro-phenol or *m*-dinitro-benzene with a water-bath, and iodoform or phenyl glucosazone with a glycerine bath.

The greatest care is necessary when using sulphuric acid. If it becomes discoloured add a *small* crystal of potassium nitrate.

III. Another method, for use with larger quantities of substance, is to fit up the apparatus shown in Fig. 93. Into the inner tube put some of the

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solid and carefully melt it. The liquid should cover the bulb of the thermometer and should be heated to some 10° above the melting-point. Fit the apparatus together and take the temperature every 15 or 30 seconds. When the melting (freezing) point is reached, the temperature will remain steady for some time (owing to the latent heat of solidification), and then will fall again. A time-temperature curve will clearly show the melting-point. Fig. 94 shows such a curve for naphthalene.

B. **Boiling-point.**—I. When sufficient substance is available it is placed in a small distilling-flask and a thermometer with as much of the stem as possible inside the flask is fixed into the cork. If the liquid boils below 150° a Liebig's condenser is attached; if above 150° an air-cooled condenser will do. The thermometer bulb must not dip into the liquid.

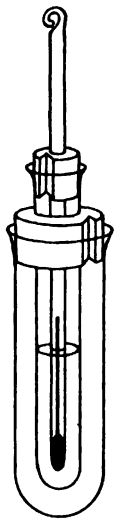

FIG. 93.

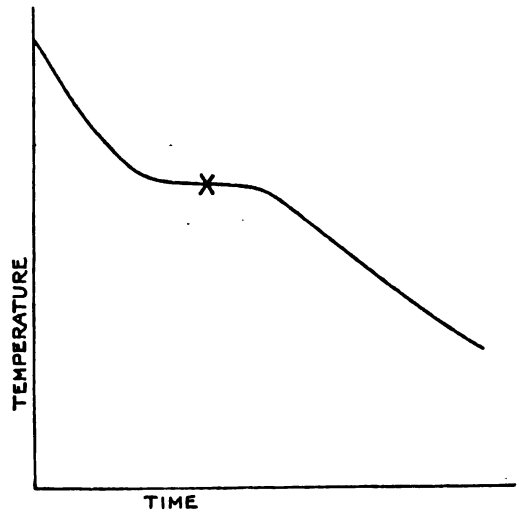

FIG. 94.

II. When very small amounts are available the vapour-pressure method may be used. A U-tube, as shown in Fig. 95, is closed so that the end is rounded neatly off. Introduce a little of the liquid through the open limb, and then enough mercury to fill the open limb. By a little manipulation all air is removed from the closed end and about half a cm. of the liquid can be made to stand on the mercury in the closed limb. Immerse the U-tube with a thermometer in a suitable bath and heat the bath-liquid, stirring well. When the boiling point is reached the liquid will vaporise and depress the mercury in the closed limb till the surfaces in both limbs are at the same level. Note the temperature carefully at which they become level. On further heating the mercury surface in the open limb will rise above that in the closed limb. Hence let the bath cool again, and note the temperature at which the surfaces become level again. Correct for the exposed stem of the thermometer as before.

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III. *Siewoboloff's method* (B. **19**, 795) is approximate only (Fig. 96). It is carried out by placing a few drops of the liquid in the small glass tube *a* which is fastened to a thermometer as shown. A glass capillary sealed about 1 cm.

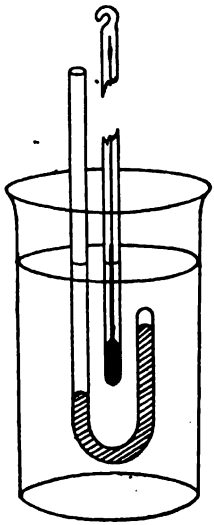

FIG. 95.

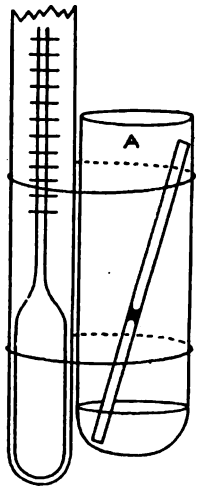

FIG. 96.

from the lower end is introduced, and the tube heated in a bath. Air bubbles escape slowly from the capillary. At the boiling-point a rapid stream of bubbles is emitted, apparently from this capillary. Take several readings, each with a fresh capillary.

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CHAPTER III.

PREPARATION OF TYPICAL ORGANIC COMPOUNDS.

THE preparation of some of the most important compounds directly from natural sources will first be dealt with. General methods, synthetic methods, etc., will follow.

PREPARATION 1.

Methyl alcohol, acetone and acetic acid from wood spirit.

Small pieces of wood are put into an iron retort of about 2 litres capacity, fitted with a screwed-in lid and delivery-tube. Failing this an iron tube of about 2 inches bore may be used, but a tube-furnace will be necessary to heat it. The delivery tube leads to a receiver cooled under the tap, and a tube from the receiver to the draught. Heat carefully, raising the temperature slowly to 300-400°. An aqueous and a tarry distillate will collect in the receiver and inflammable gases, which should be ignited, come off. When enough distillate has collected (not less than 250 c.cs.), the watery layer is separated from the tar. The former contains water, methyl alcohol, acetic acid, methyl acetate, etc. It is just neutralised with NaOH and distilled. The distillate contains methyl alcohol, acetone, etc., and the residue sodium acetate. This residue is dried, treated with strong sulphuric acid, and carefully distilled. Glacial acetic acid collects in the receiver.

To the distillate containing the methyl alcohol, etc., anhydrous calcium chloride is added. This produces a crystalline compound, $CaCl_2$, $4CH_3OH$. As much of this as possible is filtered off on the pump and the filtrate distilled on the water-bath, when impure acetone collects in the receiver. It may be purified as under acetone, pp. 312 and 324.

N.B.—The acetone of commerce is prepared mostly from acetates obtained from wood spirit.

The calcium chloride compound of methyl alcohol is decomposed by distilling it with water, the aqueous methyl alcohol being dehydrated by quick-lime and distilled.

PREPARATION 2.

Ethyl alcohol, C_2H_5OH.

In commerce this may be obtained from potatoes by heating them under pressure to 150° C., and then fermenting with malt and yeast. The starch is thus converted into sugar (dextrose, etc.) by hydrolysis, and this into alcohol by the yeast.

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The fermentation is a very complex and imperfectly understood process, and no attempt is made to give an equation.

In the laboratory, alcohol may be made by fermenting dextrose or sucrose by yeast at a temperature of 36° C. in not too strong a solution. The product is distilled, and the portion coming over below 95° is fractionated. Alcohol of about 90 % results: it may be dried by distilling from quick-lime. If desired, a small quantity of "fusel oil" (higher alcohols) can be removed by stirring well with 70 % of its weight of charcoal and standing for several days before dehydrating with lime.

Preparation 3.

Lactic and butyric fermentation of sugar. A. A. Claflin, *J.S.C.I.*, 1897 (16), 516. H. Emde, *Milchsäure*, Dammer's *Chemische Technologie der Neuzeit*, I. 674 (1910).

Preparation of fermentation lactic acid, $CH_3 . CH(OH) . COOH$.

A litre of a 10 % solution of glucose or sucrose is made, and 1 % of ammonium nitrate added. Boil, cool to 55°-45° C., and add about 100 c.c. of milk that has stood at 45° till quite sour. The temperature is kept between the above limits to prevent the formation of butyric ferments; from time to time chalk-dust or zinc oxide suspended in water is added in such quantities as to keep the liquid just acid. This proceeds for a few days. To stop the action of the ferments heat quickly to boiling, filter and evaporate to crystallisation. Add any crusts of calcium or zinc lactate to the crystals, and recrystallise the whole. Decompose the salts by dissolving in water and adding the calculated amount of sulphuric acid of sp. gr. 1·25. Calcium sulphate is filtered off and the lactic acid concentrated *in vacuo* to a sp. gr. of 1·2. Zinc sulphate is got rid of by extracting the lactic acid with ether, which is distilled off, or hydrogen sulphide is passed through the zinc *lactate* solution to saturation, the zinc sulphide filtered and the filtrate concentrated as above. The inactive or racemic form of the acid is left as a thick, sour liquid.

Preparation of butyric acid, $CH_3 . CH_2 . COOH$.

A similar sugar solution to that described above is warmed to 25°-35° C. To it is added a small piece of rancid butter or cheese, a little ammonium nitrate as food for the ferment, and enough calcium carbonate in suspension to keep the solution neutral. After standing as above, heat to boiling, filter and treat the calcium butyrate with sodium carbonate. Filter off the pptd. calcium carbonate, render acid with sulphuric acid (S.G. 1·25), and distil the product. If preferred, the zinc salt may be made instead of the calcium salt, and treated as described for zinc lactate. The acid is a liquid with a characteristic smell. B.P. 162°.

Saponification of Fats and Oils.

Preparation 4.

Soaps, Stearic and Oleic acids.

200 gms. of beef or mutton fat are melted on a water-bath, filtered through muslin to remove tissue, and poured into 200 c.c. of 96 % alcohol in a 2-litre

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flask at a temperature of 30°. 90 gms. of NaOH are dissolved in a *little* water, and while still hot, added, a little at a time, to the alcoholic fat. A violent action follows each addition of the soda, and the mixture is well shaken. The product is soluble in water. The alcohol is evaporated off on a water-bath, and the product dissolved in hot water. Saturated brine is added to the soap solution thus obtained, and the resulting ppt. collected and washed with a little water.

The above method is much quicker than saponifying with aqueous soda, which takes a very long time on the small scale.

The crude mixture of acids is given by pouring a portion of the soap solution into slightly diluted hot hydrochloric acid, allowing the oil to set, removing it as a cake and washing with water.

Purification of the crude acids thus obtained.

Dissolve the cake of crude acids in 4-5 times its weight of alcohol. Make a solution of magnesium acetate by dissolving 8 gms. of magnesium oxide in 100 c.c. of 25% solution of acetic acid in alcohol for every 100 gms. of the crude acid. Mix the two solutions, stir, filter off the ppt. of magnesium stearate and wash with a little alcohol. Repeat the pptn. with similar amounts of magnesium acetate twice more from the *filtrate*, and wash as before. The first portion of the ppt. will be fairly pure magnesium stearate, the third, impure magnesium oleate. Boil up each ppt. with dilute hydrochloric acid, allow the molten acid to set, and recrystallise the stearic acid from alcohol. Its M.P. should be between 65° and 70° (pure 71°). The impure oleic acid is dissolved in alcohol and digested on a water-bath with litharge. The solution is filtered and treated with HCl to set free the acid, which is recrystallised. M.P. 14°.

5. Preparation of Glycerine from the Soap Lyes.

The solutions from which the soap has been salted out are called "soap lyes." They contain glycerine formed as already indicated. This is obtained by neutralising, filtering and evaporating under reduced pressure. The residue, filtered through muslin from the deposited salts, is impure glycerine, which is purified by distilling with steam under pressure and evaporating the distillate under reduced pressure. The method is not often worked in the laboratory.

Preparation 6.

Sucrose from beet-root.

500 gms. of sugar-beet, cut into small pieces about 2 mm. thick, are extracted with water kept at 80°-90°. This is conveniently done by boiling under a reflux condenser under slightly reduced pressure for 30 minutes. Filter and warm the filtrate with a little milk of lime (about 8 gms. of lime), whereby the acids are neutralised, and iron and magnesium, etc., salts pptd. Filter, and pass carbon dioxide into the warm solution. Filter from the ppt. of calcium carbonate and concentrate by evaporating under diminished pressure. If preferred this may be done by distilling *in vacuo*, heating on a water-bath. A thick syrup is obtained which takes some time to crystallise. The mother-liquor may be used for the next preparation.

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Preparation 7.

Glucose from sucrose.

Make a 10 % solution of sucrose in 90 % alcohol, and add 10 c.c. of strong hydrochloric acid to each 100 c.cs. of solution. Warm for some time on a water-bath and cool. The sucrose is thereby "inverted."

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}.$$

Glucose being less soluble in alcohol than fructose crystallises on cooling or evaporating the alcohol. Further purification may be carried out by fractional crystallisation, which, however, is very tedious owing to the slowness of crystallisation.

Preparation 8.

Lactose from milk.

Milk is coagulated by the addition of rennet at 30° C. (10 c.cs. of rennet to a quart of milk). It is set aside to coagulate. The curd is well broken up with a glass rod and strained off through a cloth. The whey is then filtered if necessary and evaporated on a water-bath to crystallisation. Lactose crystallises with one molecule of water. It may readily be purified by recrystallisation. The properties of lactose are fully described in the chapter on reactions in the carbohydrate group.

Preparation 9.

Oxalic acid from carbohydrates.

Warm 150 gms. of nitric acid, S.G. 1.32 to 50° C., in a large flask in the fume-cupboard. Add carefully and gradually 30 gms. of cane-sugar; a violent action ensues and torrents of nitrogen peroxide are evolved. When finished, evaporate to one-third of its bulk, and set aside to cool. Remove the crystals which form by filtering through glass-wool and recrystallise from water.

Another method, following commercial practice more closely, is to heat a mixture of 50 parts sawdust, 40 parts caustic potash, and 60 parts caustic soda to 240-260° for 7 hours in an iron pan. Boil the cold residue with 250 c.cs. of water, decant, filter through glasswool, and add enough calcium chloride to the boiling solution, which has been made acid with acetic acid, to ppt. all the oxalates as calcium oxalate. The ppt. is filtered, washed with dilute acetic acid, then with water, dried and weighed. It is then boiled for 15 minutes with the right amount of 4N sulphuric acid, allowed to stand overnight, filtered from the calcium sulphate and evaporated to crystallisation.

Preparation 10.

Malic acid from unripe apples.

The juice is pressed out of the fruit by a press, warmed, filtered and heated gently with not quite enough milk of lime to neutralise it (litmus). The ppt. is treated with boiling dilute nitric acid (1 acid : 10 water). On cooling calcium mono-malate crystallises out. This is crystallised from water, and

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lead acetate added to its aqueous solution. The pptd. lead salt is suspended in water and treated with hydrogen sulphide to obtain the acid, which is evaporated *in vacuo*. Properties: crystals, S.G. 1·56, M.P. 100°; rather insoluble in alcohol and water. At 120° it is transformed into fumaric acid, and at 175°-180° into maleïc.

Preparation 11.

Tartaric acid from "argol."

In wine-making, the acid potassium tartrate present in the grape-juice is rendered insoluble by the alcohol and separates as a brown powder. To obtain tartaric acid from it, boil with water and chalk. This ppts. calcium tartrate, leaving potassium tartrate in solution. Add calcium chloride to the boiling liquid till no more calcium tartrate is pptd., filter and treat the calcium tartrate with the right amount of dilute sulphuric acid to decompose it, leave overnight to allow the calcium sulphate to crystallise, filter, evaporate filtrate to one-third and set aside to crystallise.

Preparation 12.

Citric acid from lemons.

Heat nearly to boiling the filtered juice of three or four lemons, and run in a suspension of chalk in water, with constant stirring, till neutral. Calcium citrate, insoluble in hot water, is pptd. Filter, wash with hot water, decompose with dilute sulphuric acid (avoiding excess), filter when cold and concentrate to crystallisation.

Preparation 13.

Urea from urine.

To a litre of urine add 250 c.cs. of a mixture of 1 vol. of saturated barium nitrate solution and 2 vols. of saturated barium hydroxide solution. Stir well, filter off the phosphates, sulphates, etc., and evaporate to a thick syrup. This contains urea, chlorides, creatinine and organic salts. Treat with 300 c.cs. of 95 % alcohol and filter. The filtrate now contains pigmented urea, from which the colouring matter may be removed by boiling with animal charcoal, filtering and crystallising. From this urea good crystals of urea oxalate may be made by adding to its strong solution in water a strong solution of oxalic acid. The oxalate, $2CO(NH_2)_2$, $C_2H_2O_4$, H_2O, is deposited.

Preparation 14.

Uric acid from guano.

Boil the guano with caustic soda till no more ammonia is evolved, filter and add a few c.cs. of concentrated hydrochloric acid (more than enough to neutralise the caustic soda). The uric acid is deposited on standing.

Preparation 15.

Hippuric acid, $C_6H_5 . CO . NH . CH_2 . COOH$.

To a litre of the urine of a herbivorous animal (horse or cattle) add excess of milk of lime and boil. Filter while hot and concentrate the filtrate. Cool

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and acidify strongly with concentrated hydrochloric acid. Set aside and filter off the crystals of hippuric acid which separate. To purify, wash them with a *little* cold water and dissolve in hot water. Run this solution through a mass of animal charcoal in a funnel and wash through with hot water. Filter and concentrate. The acid prepared in this way cannot be quite freed from a slight smell connected with its source. The pure acid must be synthesised. M.P. 187°.

Preparation 16.

Benzoic acid and glycine from hippuric acid.

Benzoic acid, C_6H_5COOH, is prepared from hippuric acid by hydrolysing with strong hydrochloric acid. A strong solution of hippuric acid is treated with four times its weight of strong hydrochloric acid and boiled for an hour in a flask with a reflux condenser. It is then allowed to cool and the benzoic acid which separates is recrystallised from hot water. The filtrate is evaporated to crystallisation, when glycine hydro-chloride forms. It is washed on the filter with a little ether to free from benzoic acid. The free acid is made from the hydrochloride by preparing the lead salt by treatment with freshly pptd. lead hydroxide, filtering off the lead chloride and saturating the filtrate with hydrogen sulphide. The lead sulphide is filtered off and the filtrate evaporated. Glycine is a thick liquid which crystallises to large colourless crystals, soluble in water, not soluble in alcohol or ether. It melts at 236° with decomposition. It gives a red coloration with ferric chloride. See p. 334.

Preparation 17.

Tyrosin (p-oxyphenyl-α-aminopropionic acid) from silk waste.

$$OH.C_6H_4.CH_2.CH(NH_2).COOH.$$

Boil 40 gms. of silk waste with 120 c.cs. of strong hydrochloric acid under a reflux condenser for 6 hours. Evaporate the brown solution under diminished pressure and dissolve the residue in hot water, filter and make up to a known volume. Find the strength of the acid in a portion by titration with caustic soda. Add to the main solution the exact amount of soda necessary to neutralise it, stirring constantly and cooling with ice. Stand in iced water for an hour and filter off the tyrosin at the pump. Dissolve in hot water, boil with 4 gms. of animal charcoal and filter. Stand aside to crystallise. Concentrate the mother-liquor for a second crop. Yield, 5-6 %.

Preparation 18.

Cystine. (α-diamino-β-dithio-dilactic acid)

$$COOH.CH(NH_2).CH_2.S.S.CH_2.CH(NH_2).COOH.$$

In a litre flask boil up 150 gms. of horse-hair with 500 c.cs. of strong hydrochloric acid for 6 hours (reflux); dilute the filtered liquid with a litre of water and add concentrated caustic potash (1 in 3) till only just acid. Warm and stir with 10 gms. of animal charcoal, then filter, neutralise exactly with potash and set aside for 6 days, when crude cystine will be pptd. Filter, wash and dissolve it in a little 10 % ammonia, treat with animal charcoal and ppt. cystine from the filtrate by dilute acetic acid. Yield, about 4 gms.

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ALKALOIDS, ETC.

Preparation 19.

Nicotine from tobacco, $C_{10}H_{14}N_2$.

Boil 200 gms. of powdered tobacco with water and concentrate the filtered extract. Add excess of milk of lime or caustic soda solution and distil in steam. Neutralise the distillate with hydrochloric acid, evaporate to a small volume and make alkaline with caustic soda. Extract the liberated nicotine with ether and distil off the latter, when the nicotine will be left as an oil; B.P. 247° C. It may be dried by warming and blowing through it a current of hydrogen. Yield, about 0·5 % of the tobacco.

Preparation 20.

Quinine, $C_{20}H_{24}N_2O_2$, *from cinchona bark.*

The finely-powdered bark is mixed with slaked lime and water to a paste. This is heated to dryness on water-bath and extracted with a mixture of chloroform and ether (equal vols.). Shake the extract with successive small quantities of dilute sulphuric acid. This dissolves out the alkaloids as sulphates. Neutralise the combined solutions with ammonia, concentrate somewhat and allow to crystallise. Quinine sulphate forms first and is recrystallised to free it from cinchonine sulphate. Dissolve the quinine sulphate in water, add caustic soda solution and recrystallise the pptd. quinine from alcohol.

Preparation 21.

Caffëine, $C_8H_{10}N_4O_2$, *from tea.* (Allen, *Pharm. Zeit.*, 1897 (8) .)

10 gms. of powdered tea are boiled with 500 c.cs. of water for 6 hours (reflux). Filter the extract and dilute to 700 c.cs. Boil and remove the colour by stirring in 5 gms. of lead acetate. Filter, concentrate 600 c.cs. of the filtrate to 50 c.cs. Ppt. the excess of lead by adding sodium phosphate solution and filter. Evaporate the filtrate somewhat and extract the caffëine by successive small quantities of chloroform. Finally evaporate the combined solutions to free from chloroform. Silky needles of caffëine are left.

Preparation 22.

Indigo from urine. (*Obermayer's method*).

Though minute quantities are obtained, this process is of importance for determining the amount of indican (indoxyl-sulphuric acid, $C_8H_7NSO_4$) in the urine. Urine acidified with acetic acid is pptd. with one-tenth of its volume of basic lead acetate solution, the latter not being added in excess. Filter, and to the filtrate add an equal volume of conc. HCl containing 3 gm. $FeCl_3$ per litre to oxidise the indican. Add a few ccs. of chloroform and shake. The indigo is dissolved by the chloroform giving a blue solution which may be compared colorimetrically with an indigo solution of known strength. (See p. 394.)

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PART II.

ORGANIC PREPARATIONS—ALIPHATIC DIVISION.

CHAPTER I.

I. THE PREPARATION AND PROPERTIES OF DERIVATIVES OF THE ALCOHOLS.

1. **Rectification of methylated spirit.**—As many organic substances require alcohol for their preparation, it is necessary to be able to purify methylated spirit if nothing purer is available. If "industrial" spirit is used it is unnecessary to do more than dry it by distillation from quicklime, when it will serve for all purposes in this book where alcohol is mentioned unless it is definitely stated otherwise. If industrial spirit is not available, the spirit must be boiled with 3-4 % of caustic potash for 2 hours (reflux). This resinifies the aldehydes. The brown liquid is then distilled, stopping when the temperature reaches 80°. To dry the product, distil again after standing overnight with quicklime. It is necessary that the product should mix with water without turbidity; if it does not, hydrocarbons are present, and must be removed by calcium chloride as described for the removal of acetone under methyl alcohol, p. 293.

Properties of the alcohols.—Methyl alcohol, CH_3OH.

(1) Colourless liquid, B.P. 66° C., mobile, miscible with water, burns with a blue flame, slight odour when pure.

(2) A small piece of sodium thrown into a few c.cs. causes evolution of hydrogen, and on evaporation a white hygroscopic residue, sodium methylate, CH_3ONa, remains.

(3) Phosphorus pentachloride reacts violently, causing evolution of hydrochloric acid.

(4) If a few drops are placed in a small test-tube and a heated platinum wire is held in the tube above the liquid, the wire continues to glow in the vapour, formaldehyde, H.CHO, being produced.

(5) It is oxidised by distillation with chromic acid to formic acid. Distil a little with solid potassium dichromate and dilute sulphuric acid, and catch the distillate in another tube. Test for a formate, after neutralising with ammonia (p. 340).

(6) It will not give the iodoform test.

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Ethyl alcohol, C_2H_5OH.

(1) Colourless liquid, B.P. 78° C., mobile, miscible with water, burns, very slight odour when pure.

(2) and (3) As for methyl alcohol.

(4) If treated with chromic acid as in (5) above, a characteristic smell of acetaldehyde is obtained, CH_3CHO.

(5) To a solution of sodium carbonate add iodine till a yellow colour just persists at 50° C. and add a few drops of alcohol. A yellow ppt. with a characteristic odour, iodoform, CHI_3, appears, unless the alcohol is very dilute.

N.B.—Aldehyde and acetone also give this test.

(6) Add 1 c.c. of sulphuric acid to 1 c.c. of alcohol, and a little glacial acetic acid. A pleasant odour of ethyl acetate, $CH_3 . COOC_2H_5$, results.

2. **Preparation of alcoholates.**—Sodium methylate and ethylate are made by dissolving sodium in the *pure* alcohol and evaporating on the water-bath in a test-tube through which is passed a current of pure dry hydrogen.

Aluminium ethylate (*C.R.*, Dec. 1913; *Chem. News*, Dec. 1913).

Dip clean aluminium foil into mercuric chloride solution to amalgamate the surface. Wash with a little water, dry and dip into absolute alcohol in which some sodium has been dissolved. A grey powder, $(C_2H_5O)_3Al$, is deposited. It is decomposed by water.

3. **Preparation of Esters.**—(*a*) For general preparation of esters of organic acids, see pp. 319, 320.

(*b*) **Preparation of an acid ester and its salts.**

Ethyl hydrogen sulphate : Ethyl potassium sulphate.—To 200 gms. (250 c.cs.) of absolute alcohol, add *slowly* 150 gms. (80 c.cs.) of strong sulphuric acid. Allow the temperature to rise to 80°-90° C., and then heat on a water-bath with a reflux condenser for half an hour.

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

Cool, add ice to the liquid in a large basin, then a litre of water. Neutralise with chalk or barium carbonate. Filter the solution of calcium or barium ethyl sulphate from the calcium or barium sulphate and evaporate to crystallisation.

To obtain the potassium salt, add a strong solution of potassium carbonate to the calcium salt till the reaction is just alkaline, then a little more of the calcium salt solution till just neutral. Filter and evaporate.

If the ethyl hydrogen sulphate itself is required, add dilute sulphuric acid to the barium salt solution till no more ppt. forms; filter and evaporate in a vacuum desiccator.

Properties of $C_2H_5HSO_4$.—Oily liquid, strongly acid, soluble in water, decomposes when heated thus:

$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

(*c*) **Preparation of an inorganic ester from an alcohol and an acid or acid chloride.**

Ethyl nitrite, $C_2H_5 . O . NO$ (Dunstan & Dymond).—A cooled mixture of 32 c.cs. of alcohol, 32 c.cs. of water and 13·5 c.cs. of strong sulphuric acid is

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diluted to 120 c.cs. and dropped slowly from a tap-funnel into an ice-cooled solution of 35 gms. of sodium nitrite in 120 c.cs. of water. The nitrite should be in a tall beaker, and the alcohol mixture delivered to the bottom of the solution by standing the tap-funnel in the beaker. The ester floats up and is separated by a funnel. Distil on a water-bath after standing for a time with a little fused calcium chloride, cooling the receiver with ice. Yield, almost theoretical.

It is a pleasant-smelling liquid. B.P. 17° C.

(*d*) **Amyl nitrite** may be prepared in an exactly similar manner, using 30 gms. of amyl alcohol, 30 gms. of strong sulphuric acid, and adding it slowly to 25 gms. of potassium nitrite in 15 c.cs. of water. When added, pour in more water, separate, wash, dry and distil. B.P. 96° C. Avoid smelling the amyl nitrite as it causes dilation of the blood-vessels.

(*e*) **Ethyl sulphate, $SO_2(OC_2H_5)_2$.**—The calculated quantities of absolute ethyl alcohol and of sulphuryl chloride are weighed out. The chloride is added gradually, with cooling, through the tube of a reflux condenser to the alcohol in the flask. When added, warm to 50° C. for half an hour, wash with cold dilute sodium carbonate till free from hydrochloric acid, dry over anhydrous sodium sulphate and rectify under reduced pressure: colourless oily liquid, B.P. 208° (decomposition) at ordinary pressure. *Vapour highly poisonous.*

4. **Preparation of ethyl ether.**—(*a*) Take equal vols. of alcohol and strong sulphuric acid, and add slowly the latter to the former, cooling if the temperature rises above 80°-90°. When mixed, place in a distilling flask fitted with a tap-funnel and thermometer, and connected to a condenser fitted with an adapter, the end of which is immersed in a flask containing water and a few lumps of ice; cool the receiver with ice outside also. Warm the mixture on a sand-bath till the temperature is 140° C. Then drop alcohol in from the tap-funnel at the same rate as the liquid distils, keeping the temperature at 140° C. Stop when as much alcohol has been added as was taken originally. The receiver contains ether, alcohol and some water. Add a little salt to the distillate, shake, allow to settle and draw off the upper layer of ether. Shake it with an equal vol. of 4 % sodium carbonate to remove sulphurous acid. Separate, stand overnight with fused calcium chloride, and distil off the ether (after filtering) on a water-bath which has been heated and the flame removed.

Properties.—Colourless liquid with characteristic odour. B.P. 35° C. S.G. 0·736.

For some purposes pure dry ether is required. Traces of water and alcohol are removed by adding small pieces of sodium till no further action takes place, and distilling again.

(*b*) **Williamson's method.**—Any ether may be made in this way, including mixed ethers.

$$C_2H_5ONa + C_2H_5I = NaI + (C_2H_5)_2O.$$

Place 50 c.cs. of alcohol in a flask fitted with a reflux condenser and standing on a water-bath. Dissolve 3 gms. of sodium in it, and then add 17 gms. of ethyl iodide. Heat till sodium iodide is deposited, then distil. Purify as in (*a*).

Ethyl-propyl ether may be made similarly by using a corresponding amount of propyl-iodide instead of ethyl-iodide.

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5. **Ethylene, C_2H_4, and Ethylene bromide, $C_2H_4Br_2$.**—In a 2-litre flask place a little sand (to prevent frothing) and a mixture of 90 c.cs. of strong sulphuric acid and 30 c.cs. of alcohol. Heat till the gas is evolved.

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O,$$
$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

Drop in from a tap-funnel a mixture of equal vols. of alcohol and strong sulphuric acid. The gas is firstly washed with concentrated caustic soda and then led into bromine in two absorption vessels as shown in Fig. 97. The first contains 40 gms. (13 c.cs.) of bromine and 4 c.cs. of water; the second 12 gms. (4 c.cs.) of bromine and 1 c.c. of water. A vessel of soda-lime is attached to the second bottle to prevent the escape of bromine. If necessary renew the soda in the wash-bottle and if the contents of the generator char badly, a fresh mixture should be taken. After a few hours the bromine becomes a pale straw colour. Shake up the contents of the two bottles with an equal vol. of dilute caustic soda in a separating funnel and run off the heavy oily layer, wash it with water, separate again and warm it with fused calcium chloride. Filter and fractionate. Take the distillate at 130°-132° C.

Colourless liquid, solidifying to white crystals at 9·5°, S.G. 2·18 at 18°.

Preparation of halogen derivatives from alcohols.

6. **Ethyl chloride by direct esterification.**—(*a*) In a flask place 10 gms. of common salt and 20 c.cs. of alcohol. Fit the flask with a tap-funnel and an upright condenser, from the top of which a tube leads to a U-tube immersed in a freezing mixture. Hence a tube leads to an absorption vessel for excess of HCl. Drop slowly in from the tap-funnel 10 gms. of strong sulphuric acid, and warm on the water-bath. Keep water at 15°-20° C. circulating round the condenser. Ethyl chloride collects in the U-tube. B.P. 12° C. It should be preserved in a sealed tube.

(*b*) **Grove's process.**—Pass a rapid stream of hydrochloric acid gas through a small empty flask and then through a flask containing 100 c.cs. of alcohol and 40 gms. of zinc chloride, standing in a water-bath. The empty flask is to prevent alcohol from being drawn into the generator. The alcohol is warmed gently whilst the gas is passing. The rest of the apparatus and procedure are the same as in (*a*).

7. **Ethyl bromide by direct esterification.**—To 60 gms. of 95 % alcohol add slowly, with constant stirring, 120 gms. (66 c.cs.) of strong sulphuric acid. Cool the flask to the room temperature and add slowly (1) 30 gms. of ice; (2) 60 gms. of powdered potassium bromide. Connect with a Liebig condenser fitted with an adapter, the end of which dips under water and ice in the receiver. Distil fairly quickly, keeping the receiver at 0° C. As soon as oily drops cease to collect below the water in the receiver, stop the reaction and separate the product from the water in the receiver. Shake it with

(1) successive quantities of water;
(2) dilute sodium carbonate

in a separating funnel, keeping the funnel open in (2) to permit the escape of CO_2. Then stand overnight with calcium chloride in a closed vessel in a cool

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place. Filter and distil off the ethyl bromide on a water-bath kept at 60°-70°. Collect the portion coming over at 37-40° C. Seal up in a glass tube. Yield, 40-50 gms.

8. **Any bromide.**—In a flask of suitable size place a mixture of the calculated amounts of the alcohol (in this case 75 c.cs. of 95 % alcohol) and red phosphorus (10 gms.). The required amount of bromine is then run slowly in from a tap-funnel (22 c.cs. here) with constant cooling and shaking. Leave the mixture overnight and distil off the ethyl bromide from a water-bath as in (*a*) above, having a soda-lime tower attached to the receiver to absorb hydrobromic acid fumes. Purify as before.

Reaction: $PBr_3 + 3C_2H_5OH = P(OH)_3 + 3C_2H_5Br$.

N.B.—With higher bromides the procedure is slightly modified to suit the higher boiling-point, etc. See next preparation.

Properties of ethyl bromide.—(1) Colourless liquid, B.P. 38° C., insoluble in water, soluble in alcohol or ether. S.G. 1·45 at 15° C.

(2) Should give no ppt. with $AgNO_3$, but on addition of nitric acid and heat a ppt. of AgBr slowly forms.

(3) Heated with alcoholic potash, is decomposed into the olefine and HBr(KBr).

$$C_2H_5Br + KOH = KBr + H_2O + C_2H_4.$$

9. **Preparation of secondary butyl bromide** (Freundler, *Bull. Soc. Chim.* (3), xxxv. p. 110).

$$CH_3 . CH_2 . CHBr . CH_3.$$

To 26 gms. of secondary butyl alcohol add slowly 5 gms. of PBr_3 or the corresponding amounts of red phosphorus followed by bromine, as in (*b*). Keep the temperature below 10° C. Leave overnight, warm on water-bath for half an hour (reflux), when the liquid separates into two layers. Wash as above, dry and rectify.

N.B.—When preparing the higher bromides, it is advisable to use phosphorus bromide if obtainable, instead of phosphorus and bromine as the bromide often forms a kind of emulsion with the excess of phosphorus (if any) and water, this emulsion being difficult to handle.

10. **Preparation of iodides.** *Ethyl iodide by phosphorous iodide method.*—This is in most respects similar to the preparation of ethyl bromide, except that the iodine is dissolved in as much of the alcohol as is necessary, so that it can be added through the funnel. In the flask put 10 gms. of red phosphorus and as much of the 75 c.cs. of alcohol as may be necessary to dissolve the iodine. Use 100 gms. of iodine. Heat the reaction mixture with a reflux condenser on the water-bath for 2 hours before distilling. B.P. 72°.

Properties.—1. Colourless liquid when pure; usually coloured with iodine. B.P. 72°; S.G. 1·95 at 15°. Insoluble in water, soluble in alcohol and ether.

2. On shaking with silver nitrate solution, silver iodide is slowly pptd., assisted by warming. (Note difference from ethyl bromide.)

3. Warmed with alcoholic potash, ethylene and potassium iodide are produced. (See preparation 7, page 309).

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Preparation of trihalogen derivatives.

11. **Chloroform, $CHCl_3$.**—Into a 2-litre round-bottomed flask put a mixture of 150 gms. of good bleaching powder and 300 c.cs. of water, ground to a cream. Rinse into the flask with another 300 c.cs. of water and add 50 c.cs. of acetone or alcohol. Connect the flask to a condenser and receiver, and warm on a water-bath. If the reaction becomes too vigorous, cool the flask in a bowl of water. Finally distil from a sand-bath till no more oily drops collect. Separate the chloroform, shake it with very dilute (1 %) caustic soda, separate again and stand in a corked distilling flask with some calcium chloride till quite clear. Distil from a water-bath. B.P. 61°.

Properties.—1. Colourless liquid; characteristic odour. S.G. 1·5. Almost insoluble in water, soluble in alcohol.

2. Dissolves iodine to give a purple solution.

3. Warmed with alcoholic potash it is hydrolysed to formic acid, which may be detected by the silver mirror test.

$$CHCl_3 + 4KOH = H.COOK + 3KCl + 2H_2O.$$

4. A *few drops* warmed with 2 c.cs. of alcoholic potash and a drop of aniline give the penetrating and disagreeable odour of phenyl carbamine (iso-cyanide).

$$CHCl_3 + C_6H_5.NH_2 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$

(Pour down sink and flush with water as soon as observed.)

5. Burn a mixture of chloroform and alcohol (1 or 2 c.cs.) in a small dish. Note the green-edged flame characteristic of halogen derivatives.

12. **Bromoform, $CHBr_3$** (Muller & Loebe, *Zeit. Elect.*, 1904, **10**, 409).—Electrolyse a mixture of 60 gms. of potassium bromide, 150 c.cs. of water, 0·3 gms. potassium chromate and 20 c.cs. of acetone, with a current of 3 amps. at 4 volts for 4-5 hours.

The cell is a beaker of 200 c.cs. capacity cooled in a bath of water. The anode is a cylinder of sheet platinum bent to fit closely inside the beaker, and having an area of 50 sq. cm. The cathode is a spiral of stout platinum wire in the centre of the cell. The temperature must not rise above 20°, and the potash produced at the cathode is neutralised by a *rapid* stream of carbon dioxide from a tube passing to the bottom of the cell, which also serves to keep the solution well stirred.

Separate the bromoform, free it from dissolved bromine by shaking in a separating funnel with dilute sodium carbonate and acetone. Dry over calcium chloride and distil. B.P. 151°.

Properties.—M.P. 7·6°; S.G. 5·9°.

Chemically, closely resembles chloroform, except that potassium bromide instead of chloride is formed in the reactions described.

13. **Iodoform, CHI_3.**—Dissolve 10 gms. of sodium carbonate (anhydrous) in 50 gms. water. Warm to 60° and add 7 c.cs. of alcohol and about 10 gms. of iodine, until a permanent brown colour is produced. Discharge this with a few drops of the soda solution kept back for the purpose, warm to 70°, and set aside till cold. Filter off the yellow ppt. of iodoform and recrystallise it by dissolving in 20 c.cs. of ether, shaking in a separating funnel with

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water, separating, drying the ether solution over calcium chloride and then allowing it to evaporate in a draught-cupboard away from all lighted burners. Test its M.P.

Properties.—1. Yellow leaflets; characteristic odour; M.P. 119°; insoluble in water, soluble in alcohol and ether.

2. Alcoholic potash; similar to chloroform, but potassium iodide is produced.

3. On heating, it melts and decomposes, liberating iodine.

The iodoform test is given by ethyl alcohol, aldehyde and acetone (see p. 301). Even if the precipitate is not always produced in very dilute solution, yet the characteristic odour may be obtained.

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CHAPTER II.

SUBSTITUTION AND ELIMINATION OF HALOGEN IN HALOGEN DERIVATIVES.

1. **Substitution by hydroxyl. Hydrolysis.**—The ease with which this can be done varies greatly. Monohalogen derivatives are difficult to hydrolyse, whilst di- and tri-derivatives are readily acted on by heating with *aqueous* alkalis. *Alcoholic* potash always removes the halogen together with hydrogen from the next carbon atom, giving unsaturated derivatives.

The best methods for mono-derivatives are:

(*a*) *Direct method.*—Boil for an hour with water (reflux) and freshly-pptd. and washed silver oxide or lead hydroxide. Filter from pptd. chloride, etc., and fractionate the product, finally dehydrating and distilling over quicklime. (*b*) *Indirect method.*—Mix the iodide with the calculated quantity of silver acetate and a little ether. Warm (reflux), separate the ester by distillation and hydrolyse by boiling with potash solution (reflux). Finally distil and dry the alcohol as in (*a*).

As an example of the ease of hydrolysis of a dihalide, we will take the

Preparation of glycol from ethylene dibromide (Wurtz, *C.R.*, **43**, 194. Haworth & Perkin, *J.C.S.*, **69**, 175).—Into a 250 c.c. flask put 25 gms. of ethylene di-bromide, 20 gms. of dry potassium carbonate, and 120 c.cs. of water. Boil (reflux) for some hours till the bromide layer has disappeared. (Add more reagents and continue if desired.) Finally distil the aqueous solution. The glycol comes over with the steam. Distil the product *in vacuo*, when glycol will be left as a thick syrup.

Properties.—B.P. 195. Sweet taste; soluble in alcohol and water, but not in ether.

2. **Substitution by Hydrogen. Preparation of Ethane.**—By reduction of the corresponding mono-halide.

Pour dilute copper sulphate solution on to 20 gms. of granulated zinc. Decant and repeat twice as the colour is discharged. Wash the zinc-copper couple with water. Place in a 250 c.c. flask fitted with tap-funnel and delivery tube. Slowly drop in a mixture of the iodide and alcohol, when a stream of the gas is evolved. Collect over water.

3. **Replacement by $-NH_2$, giving amines.**—When the halides are heated in sealed tubes with alcoholic ammonia to 100°, mixtures of 1^{ry}, 2^{ry}, and 3^{ry} amines are produced, also some quaternary ammonium salt. The separation is long and tedious and other methods of preparing each kind of amine separately are preferred.

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4. **Replacement by – CN, giving nitriles.**—This reaction is of great importance, enabling one to introduce another C atom and so pass up an homologous series.

(*a*) **Preparation of succino-nitrile, $CN.(CH_2)_2.CN$.**—Fit a 500 c.c. flask with a reflux condenser and in it place a solution of 50 gms. of Ethylene dibromide in 75 c.cs. of alcohol. Warm gently on a water-bath, and add gradually through the condenser tube 250 c.cs. of a cold concentrated aqueous solution of potassium cyanide. Boil for 2 hours, cool, decant from the potassium bromide and evaporate in a distillation apparatus under reduced pressure, heating on a water-bath. The residue is taken up in alcohol, the alcohol distilled off, and the residue fractionated under reduced pressure.

B.P. 147° under 10 mm. pressure.

(*b*) **Preparation of aceto-nitrile, CH_3CN.**—Dissolve 50 gms. of ethyl bromide in 75 c.cs. of alcohol in a flask fitted with a reflux. Boil on a gently-heated sand-bath and slowly add 200 c.cs. of concentrated potassium cyanide solution. Boil for an hour, cool, decant from the potassium bromide and distil. To the distillate add saturated potassium carbonate solution, followed by solid carbonate till no more will dissolve. The nitrile separates as the upper layer. Separate, dry over calcium chloride and distil. B.P. 82°.

Properties.—1. Colourless liquid with characteristic smell. B.P. 82°.

2. Boiled with sulphuric acid (1 : 1) for an hour (reflux) it is hydrolysed to acetic acid and ammonia.

(*c*) **Alternative method** (Guillemard, *Ann. Chem.*, **14**, 363 (1908).—Heat 7·5 gms. of ethyl iodide and 3·1 gms. of pure KCN to 250° for 16 hours in a bomb-tube (see Carius' *Method of Estimating Halogens, etc.*). When finished the contents are mixed with 20 c.cs. of water in a flask (the tube being washed out with 2 c.cs. of alcohol and added to the main solution). Add 2 c.cs. of lime-water and distil.

Yield about half the weight of cyanide used.

5. **Replacement by $-NO_2$, giving nitro-paraffins and nitrites** (Victor Meyer, *A.* 1874, **171**, 18).—The iodide is treated with silver nitrite.

(*a*) *Preparation of silver nitrite.*—Dissolve 25 gms. of silver nitrate in 25 c.cs. of water and add 15 gms. of potassium nitrite in 40 c.cs. of water. Stir well, cool, filter off the pptd. silver nitrite, wash well with ice-cold, small quantities of water and dry in a desiccator in the dark.

(*b*) *Preparation of nitro-ethane.*—Put 20 gms. of silver nitrite in a 100 c.c. round-bottomed flask fitted with a dropping funnel and a reflux condenser. Add slowly 16 gms. of ethyl iodide. Do not allow it to boil too violently. When all is added, warm on a water-bath and then distil all that comes over below 100°. Return this to the reaction flask and heat it again. Return the distillate once more and distil again. The nitro-ethane comes over at 110°-114°, the ethyl nitrite at 18°.

Properties of nitro-ethane.—1. Liquid, colourless when pure. B.P. 113°-114°; S.G. 1·06 at 13°.

2. Easily soluble in alkalis, forming a "salt." Nef (1894) showed that this had the constitution

$$C_2H_4 = N\begin{cases} ONa \\ O \end{cases}$$

and that the nitro-paraffin is a *pseudo-acid*.

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3. If potassium nitrite be added to the alkaline solution, followed by dilute sulphuric acid drop by drop, a red colour is obtained, due to the potassium salt of a *nitrolic acid*

$$CH_3 . CH_2 . NO_2 + O : NOH = CH_3C\begin{matrix} \diagup\!\!\diagup NOH \\ \diagdown NO_2 \end{matrix} + H_2O.$$

Similarly treated, a *secondary* nitro-paraffin gives a blue compound, soluble in chloroform, known as a *pseudo-nitrol.*

$$(CH_3)_2 . CHNO_2 + HONO = (CH_3)_2 . C\begin{matrix} \diagup NO \\ \diagdown NO_2 \end{matrix} + H_2O.$$

Tertiary nitro-paraffins do not react at all with nitrous acid.

V. Meyer employed these reactions to distinguish between 1ry, 2ry and 3ry *alcohols* (*via* the halide and nitro-paraffin).

N.B.—Methyl iodide and silver nitrite give chiefly nitro-methane.

Ethyl iodide gives about equal amounts of each. Higher iodides give less and less nitro-paraffin and more and more nitrite.

6. **Replacement by alkyl groups.**—Wurtz's reaction. *E.g.*

$$2CH_3I + 2Na = C_2H_6 + 2NaI.$$

The reaction is carried out quantitatively by dropping small pieces of sodium into the ethereal solution of the halide. Collect the gas over water.

7. **Removal of hydrogen halide from a halogen compound.**

$$\text{Preparation of} \left\{ \begin{matrix} \text{Ethylene} \\ \text{Acetylene} \end{matrix} \right\} \text{from} \left\{ \begin{matrix} \text{Ethyl} \\ \text{Ethylene} \end{matrix} \right\} \text{bromide.}$$

Arrange a distilling flask on a sand-bath. Fit it with a tap-funnel and a condenser sloping upwards. Attach the upper end of the condenser to a delivery-tube leading to a pneumatic trough. In the flask place 75 c.cs. of concentrated methylated spirit solution of potash. Warm gently and slowly drop in the halide from the funnel. The gas evolved is collected in the usual way.

Properties of acetylene.—1. Colourless gas, burns with lurid smoky flame (intense white flame when a proper burner is used). Very explosive when mixed with air.

2. Gives ppts. with ammoniacal solutions of cuprous chloride (red) or silver oxide (white) which are very explosive when dried. The copper salt has the formula Cu_2C_2 when dry and regenerates acetylene when warmed with acid.

3. Shaken with bromine water or alkaline permanganate, the reagent is decolorised.

Note.—The usual preparation of acetylene from calcium carbide gives a very impure gas. It may be purified *via* the copper compound as above.

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CHAPTER III.

OXIDATION PRODUCTS OF ALCOHOLS.

THE oxidation of alcohols to aldehyds or ketones is usually carried out by chromic acid. In the case of methyl alcohol, however, this is too powerful, formic acid being obtained. Formaldehyd therefore is made by oxidation with air in presence of red-hot copper or platinum.

1. **Preparation of formaldehyd, H . CHO.**—Fit two small flasks with corks, each carrying two tubes, one reaching to the bottom of the flask, the other just passing through the cork.

Connect the short tube of the first flask (which is cooled with ice) to a filter-pump and the long tube to a horizontal combustion tube about 9 inches long containing a spiral of copper or platinum wire. Connect the other end of this tube to the short exit tube of the other flask in which 40 c.cs. of methyl alcohol have been placed. Warm this flask in a water-bath to 40°, and by means of the pump draw a *rapid* stream of air through the apparatus. Heat the spiral till it glows and then remove the flame. A solution of formaldehyd in methyl alcohol collects in the receiver.

Properties.—1. A gas, B.P. $-21°$ C., with a characteristic choking smell, producing tears.

2. It is a powerful reducing agent, reducing ammoniacal silver oxide and Fehling's solution.

(*a*) To a solution of silver nitrate (10 %) add very dilute ammonia dropwise till the ppt. first formed is *not quite* redissolved. To this add some of the formaldehyd solution in a perfectly clean test-tube. Warm gently if necessary. The tube becomes covered with a brilliant silver mirror.

(*b*) *Fehling's solution* is prepared thus:

Dissolve 17 grms. of copper sulphate in 250 c.cs. of water in one bottle. In another bottle dissolve 30 gms. of caustic soda and 87 gms. of Rochelle salt in 250 c.cs. of water. Mix equal volumes of the solutions as required for use.

Any aldehyd reduces this solution (some on boiling only), giving a red ppt. of cuprous oxide.

2. **Preparation of acetaldehyd (aldehyd from 1^{ry} alcohol).**—In a 1½ litre round-bottomed flask place a solution of 100 gms. of sodium dichromate in 400 c.cs. of water. Fit to the flask a tap-funnel and bent tube leading to a condenser. The condenser is connected, by an adapter, to a receiver well cooled in ice. Warm the contents of the flask, and drop in slowly through

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the funnel a solution of 80 c.cs. of strong sulphuric acid and 150 c.cs. of alcohol. When all has run in, continue the distillation over a sand-bath. Collect about 180 c.cs. of distillate (aldehyd, alcohol, water).

Aldehyd-ammonia is prepared from this distillate as follows:

Place it in a flask and connect to the apparatus shown in Fig. 97. The receivers consist of two flasks each containing 50 c.cs. of ether. Water at about 30° is circulated through the condenser; this allows the aldehyd to pass over (B.P. 21°), but condenses most of the alcohol. The aldehyd dissolves in the ether. Now saturate the ether with ammonia gas (dried with soda-lime). Pour the ether solution into an evaporating basin and allow the ether

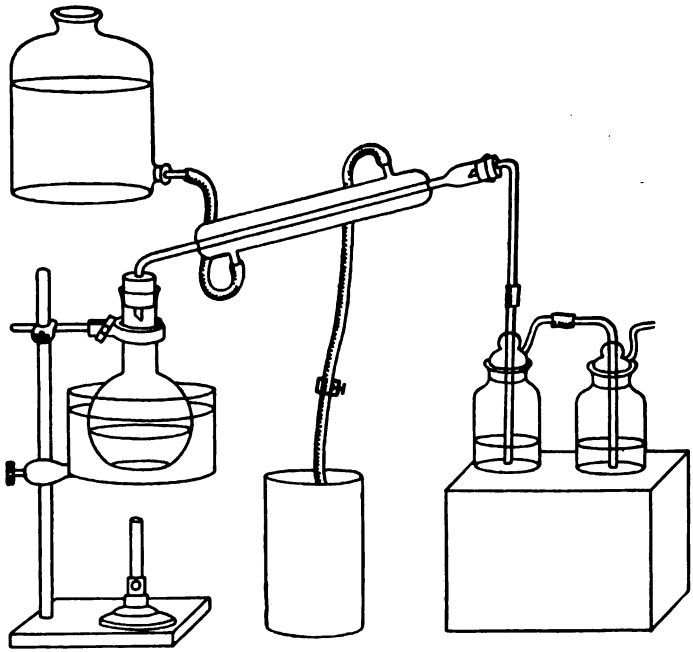

FIG. 97.

to evaporate (no lights!). Filter off the crystals of aldehyd-ammonia, wash with a very little ether, and allow to dry.

Pure aldehyd is obtained from these by dissolving them in a little water, adding to a mixture of equal volumes of sulphuric acid and water, and distilling. The receiver should be cooled with ice and salt. The distillate is dried with calcium chloride and again distilled.

Properties.—1. Liquid; colourless. B.P. 21°; S.G. ·807 at 0°. Characteristic smell; miscible with water, alcohol, ether.

2. Reduces ammoniacal silver oxide and Fehling's solutions.

3. Warmed with potash or soda a brown "resin" is obtained.

4. It restores the colour to Schiff's reagent (a solution of rosaniline hydrochloride just decolorised by sulphur dioxide).

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5. With a saturated solution of sodium bisulphite it gives a crystalline ppt. of aldehyd sodium bisulphite. (*Test for aldehyds and ketones.*)

3. **Preparation of a ketone from a secondary alcohol. Acetone from 2ry propyl alcohol.**—This is carried out similarly to the preparation of aldehyd, as far as the first distillation. The distillate is fractionated and the fraction below 60° treated with fused calcium chloride and distilled from the latter. The acetone obtained may be further purified by shaking with saturated sodium bisulphite solution and distilling the crystalline product from strong sodium carbonate solution. The product is dried by calcium chloride and rectified. B.P. 56°.

Note.—Acetone is more easily obtained by the dry distillation of calcium acetate, *q.v.* (p. 324).

4. **Preparation of acetic acid from ethyl alcohol.**—To a mixture of 15 gms. of potassium dichromate, 17 c.cs. of strong sulphuric acid and 30 c.cs. of water in a flask fitted with a reflux, add slowly a mixture of 10 c.cs. of alcohol and 25 c.cs. of water.

Boil for 20 minutes, then distil till two-thirds of the liquid have gone over. Neutralise the distillate with soda, evaporate dry and distil with a little strong sulphuric acid.

Properties.—1. Colourless liquid with pungent smell; M.P. 17°; B.P. 119°; S.G. 1·055 at 15°.

2. Warmed with a few drops of amyl alcohol and strong sulphuric acid, amyl acetate, smelling of "Jargonelle pear drops," is obtained.

3. Neutralised exactly and treated with ferric chloride, a red colour is produced, ferric acetate, which on boiling ppts. a brown basic salt.

5. **Preparation of chloral and chloral hydrate, $CCl_3 . CHO$ and $CCl_3CH(OH)_2$.** A 150 c.c. flask is fitted with a cork carrying a tube leading to the bottom of the flask, and with a reflux condenser. From the upper end of the condenser is led a tube bent twice at right angles and terminating with an inverted funnel. This dips into a beaker of strong alkali and serves to absorb excess of chlorine. The flask contains 50 c.cs. of alcohol.

Chlorine is now passed through the alcohol, which is cooled with ice at first. The chlorine should be obtained from a cylinder if one is available, as large quantities are required for this preparation.

When the absorption slackens, gradually raise the temperature on a water-bath until the boiling-point is reached, then continue to pass chlorine till no more is absorbed. Allow to cool.

$$C_2H_5OH + 4Cl_2 = CCl_3 . CHO + 5HCl.$$
$$CCl_3CHO + C_2H_5OH = CCl_3 . CHOH . OC_2H_5.$$

The solid product is chloral alcoholate. Separate and distil from concentrated sulphuric acid. Chloral passes over as an oily liquid. It is freed from hydrochloric acid, etc., by shaking with chalk and redistilling. B.P. 98°. It shows the usual aldehyd reactions.

To prepare chloral hydrate, add 10 c.cs. of water to 50 c.cs. of chloral and shake. The mixture gets hot and solidifies to a crystalline mass.

Properties.—1. Colourless crystals. M.P. 57. Easily soluble in water; pungent smell.

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2. Treated with alkali and warmed, chloroform is produced. Hence it gives the carbamine reaction. (See under chloroform.)

$$CCl_3 . CHO + NaOH = CHCl_3 + H . COONa.$$

3. It gives the usual aldehyd reactions.

4. On oxidation it forms trichloracetic acid, *q.v.* (p. 333).

6. **Reduction of aldehyds, ketones and acids.**—Aldehyds can be reduced to primary alcohols, ketones to secondary alcohols. Acids cannot be reduced directly, but the acid chloride is readily reduced. The following two methods are typical.

(i) The acid chloride or the ketone is dissolved in double its volume of ether and poured into a flask or beaker which contains some saturated potassium carbonate solution. Small pieces of sodium are added from time to time; these sink through the ethereal layer and float on the potassium carbonate solution. When a test portion of the ether layer no longer shows the reactions of ketone or acid chloride, it is separated and fractionated.

From ketones an intermediate product of higher boiling-point is produced. These are known as *pinacones*.

$$\begin{matrix} R.CO.R' \\ R.CO.R \end{matrix} + 2H = \begin{matrix} R.C.OH.R' \\ | \\ R.C.OH.R'. \end{matrix}$$

The above method may be carried out with:

Acetyl chloride	for ethyl alcohol, B.P. 78°.
Acetone	for 2ry propyl alcohol, B.P. 83°.
Methyl propyl ketone	for methyl propyl carbinol, B.P. 118°.

In the last case the main portion containing the alcohol distils at 115°-130°, whilst a pinacone comes over at 250°-260° (air condenser).

(ii) Dissolve 6 gms. of acetaldehyd or 10 gms. of butyraldehyd in 250 c.cs. of water. Then add 700 gms. of 1 % sodium amalgam in portions of 100 gms. Keep the solution just acid with dilute sulphuric acid (methyl orange).

Separate the mercury and distil the product. Again treat the distillate with 400 gms. of the amalgam as before. Distil, dehydrate the alcohol with lime. Yield, 80-90 % of theory; B.P. *n*-butyl alcohol 117·5°. Lieben and Rossi, A. **159**, 70 and 150 (1871).

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CHAPTER IV.

DERIVATIVES OF ALDEHYDS AND KETONES.

1. **Aldehyd-ammonia** has been described, p. 311.

2. **Hexamethylene-tetramine** (hexamine), $(CH_2)_6N_4$ (Delépine, A. **288**, 218).—This substance is the ultimate product of the action of ammonia on formaldehyd.

A mixture of dilute ammonia and formaldehyd is evaporated on a water-bath. More of the reagents are added as required. This reaction is of importance as giving a quick and cheap method of preparing amines.

3. **Aldehyd bisulphite compounds.**—The aldehyd is added to an equal bulk of freshly-made cold saturated solution of sodium bisulphite.

A white crystalline substance separates.

Ketones react similarly.

The original aldehyd or ketone is obtained by distillation with sodium carbonate

$$CH_3CHO + NaHSO_3 = CH_3CH\begin{cases} OH \\ SO_3Na. \end{cases}$$

4. **Polymerisation of aldehyds.**—Aldehyds, treated with concentrated sulphuric acid, polymerise to bodies having three times the molecular weight of the aldehyd, known as *paraldehyds*.

To a few c.cs. of acetaldehyd add half the volume of concentrated sulphuric acid, a drop at a time. The mixture becomes hot. When cool, add water and separate the oil which forms. B.P. 124°.

If the sulphuric acid is added at a temperature of 0°, the product is crystalline, and is known as metaldehyd. The difference is ascribed to stereo-isomerism.

Note.—These bodies do not give the aldehyd reactions. They are converted into aldehyd again on distillation from a little sulphuric acid.

Mild alkalis polymerise aldehyds to aldols.

5. **Preparation of aldol** (A. **306**, 323).—Slowly add 50 gms. of acetaldehyd to 50 gms. of ice-cold saturated potassium carbonate solution. The temperature must not be allowed to rise. Stir well after each addition, and when all is added treat with solid potassium carbonate till the liquid separates into

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two layers. Stand for several hours in ice, then extract with ether. Shake the extract with

(1) Dilute hydrochloric acid.
(2) Two small quantities of water.

Finally filter through a dry filter and dry over freshly-fused sodium sulphate. Distil off the ether, and distil the residue under reduced pressure. B.P. 79° at 15 mm.

Aldol gives the usual aldehyd reactions. It is therefore regarded as

$$CH_3CHOH . CH_2 . CH : O.$$

Ketones condense more readily than they polymerise. The condensation most easily carried out is that which results in symmetrical tri-substituted benzenes, and is important as giving a means of passing from fatty to aromatic bodies.

6. **Preparation of mesitylene from acetone.**—To 25 c.cs. of water add 50 c.cs. of concentrated sulphuric acid and cool. Then add this slowly, with cooling, to 50 c.cs. of acetone. Distil up to 170°, returning any distillate boiling under 100° to the flask. Fractionate the product after drying over calcium chloride. B.P. of mesitylene 163°.

$$3(CH_3)_2CO = C_6H_3(CH_3)_3 + 3H_2O.$$

7. **Preparation of oximes.**—These are condensation products between hydroxylamine and aldehyds (aldoximes), or ketones (ketoximes). They are of importance in isolating and identifying aldehyds and ketones.

The actual preparation varies with the aldehyd or ketone, aldoximes being more easily obtained.

(i) **Preparation of an aldoxime.**—If the aldehyd is soluble in water, to 1 molecule of aldehyd in aqueous solution add 1 molecule of hydroxylamine hydrochloride and 1½ molecules of sodium carbonate, dissolved in cold water. The oxime is obtained by extraction with ether and allowing to evaporate.

If the aldehyd is insoluble in water it is dissolved in alcohol and treated with the calculated amount of hydroxylamine hydrochloride and just sufficient caustic soda to liberate the base. Heat for 1-2 hours on the water-bath (reflux).

(ii) **Preparation of acetoxime.**

$$(CH_3)_2CO + H_2NOH = (CH_3)_2C = NOH + H_2O.$$

In a small flask place 6 gms. of caustic soda in 25 c.cs. of water and add 12 gms. of hydroxylamine hydrochloride and 12 gms. of acetone. Shake, cool, cork and stand for 24 hours. Some of the oxime separates. When no free hydroxylamine is left (test with Fehling's solution) and no excess of caustic soda remains, extract twice by shaking with equal volumes of ether. Distil off half the ether on a water-bath and let the rest evaporate. Recrystallise the product. Preserve in a sealed bottle.

Properties.—1. Needle-like, colourless crystals. M.P. 60°-61°.

2. Boiled with dilute hydrochloric acid, they are hydrolysed into their constituents. The liberated hydroxylamine may be tested for with Fehling's solution.

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8. **Preparation of hydrazones.**—Aldehyds and ketones react with phenyl hydrazine in acetic acid solution, giving crystalline bodies called hydrazones.

$$CH_3 . CHO + H_2N . NH . C_6H_5 = CH_3 . CH : N . NH . C_6H_5 + H_2O.$$

The preparation is carried out by adding to the aldehyd or ketone the calculated amount of the reagent dissolved in a mixture of 2 parts 50 % acetic acid and 3 parts of water. If the hydrochloride of the base is used, dissolve it in 10 parts of water with 2 parts of sodium acetate crystals.

The hydrazone crystallises on standing; it is then washed with dilute acetic acid and dried on a porous plate.

Bamberger recommends the use of *p*-nitro-phenyl-hydrazine hydrochloride which gives more insoluble derivatives.

9. **Preparation of osazones.**—In the case of the sugars (which are aldehyds or ketones) the use of phenyl-hydrazine is very important. Double hydrazones, called *osazones*, result, and they are of great use in identifying particular sugars owing to their widely different melting-points and characteristic appearances under the microscope. The equations are as follows:

$$\begin{array}{l} \vdots \\ CHOH + H_2N . NHC_6H_5 \\ | \\ CHO \quad + H_2N . NHC_6H_5 \end{array} = \begin{array}{l} \vdots \\ C = O \\ | \\ CH : N . NHC_6H_5 \end{array} + NH_3 + C_6H_5NH_2.$$

and then

$$\begin{array}{l} \vdots \\ C : O + H_2N . NHC_6H_5 \\ | \\ CH : N . NHC_6H_5 \end{array} = \begin{array}{l} \vdots \\ C : N . NHC_6H_5, \\ | \\ CH : N . NHC_6H_5. \end{array}$$

Phenyl glucosazone. (Typical of all these preparations).—15 gms. of glucose are dissolved in water and treated with 30 gms. of phenyl hydrazine in 30 c.cs. of 50 % acetic acid and 250 c.cs. of water (or 30 gms. of the hydrochloride with 45 gms. of sodium acetate if the free base is not available). Heat on a water-bath for about 1½ hours. Recrystallise the product from alcohol and water, or alcohol, pyridine and water. M.P. 205°.

10. **Preparation of a semicarbazone.**

$$\begin{array}{l} R \\ | \\ R \end{array}\!\!>C = O + H_2N . NH . CO . NH_2 = \begin{array}{l} R \\ | \\ R \end{array}\!\!>C = N . NH . CO . NH_2 + H_2O.$$

Aldehyds and ketones condense as above with semicarbazide, giving a typical reaction.

One gm. of semicarbazide hydrochloride is dissolved in a little water and mixed with the calculated quantity of sodium acetate. 2 c.cs. of acetone (etc.) are added (if ketones insoluble in water are used they are dissolved in alcohol, and alcohol added to clear the reaction mixture), and well shaken. The progress of the reaction varies considerably with different ketones, etc., taking from several minutes to days.

The ppt. is filtered on the pump and washed with very dilute acetic acid. Dry on a porous plate. Recrystallise from alcohol if required.

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M.P. of acetone semicarbazone, - - -	187°	(decomp.).
„ „ benzaldehyd semicarbazone - -	214°	„
„ „ aceto-acetic ester semicarbazone, -	129°	„

11. **Preparation of Acetals.**—These are condensation products of aldehyds with alcohol.

$$CH_3 . CHO + 2C_2H_5OH = CH_3 . CH(OC_2H_5)_2 + H_2O.$$

One part of acetaldehyd is mixed with 4 parts of alcohol containing 1 % of hydrochloric acid (gas). Heat is developed. After standing overnight at the room temperature the solution is mixed with an equal volume of water in which chalk is suspended. The resulting oil is extracted with ether, and the ethereal solution twice washed with water. Dry over lime and fractionate. Yield, 50 % of theory.

Properties.—1. A colourless liquid. B.P. 103°.

2. Distilled with dilute acid, it is hydrolysed to its constituents (aldehyd and alcohol).

12. **Synthesis of unsaturated acids from aldehyds.**—See Perkin's reaction, p. 387.

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CHAPTER V.

DERIVATIVES OF THE FATTY ACIDS. ESTERIFICATION.

1. **Preparation of an acid chloride. Acetyl chloride.**

$$3CH_3 . COOH + PCl_3 = P(OH)_3 + 3CH_3CO . Cl.$$

Fit a 250 c.c. distilling flask, containing 50 gms. of pure glacial acetic acid, with a cork carrying a tap-funnel. Attach a Liebig condenser and place the flask on a water-bath. The other end of the condenser is fitted to another distilling flask with a cork. This flask acts as the receiver, and the side-tube is fitted with a guard tube of calcium chloride to keep out all moisture. The water-bath contains cold water. Slowly run 42 gms. of phosphorus trichloride into the acetic acid, keeping the mixture well cooled. When all has been added raise the temperature to 50° till the evolution of hydrochloric acid gas slackens. Then boil the water and continue till nothing more distils. Redistil the product from the flask which acted as receiver, using a similar arrangement and a thermometer. Collect the portion distilling between 53° and 56°. Yield, about 40 gms.

Properties.—1. Colourless liquid. B.P. 55°; S.G. 1·106 at 18°. Fumes in air.

2. Reacts with bodies containing hydroxyl or $-NH_2$. Add a few drops to a little water in a test-tube. It sinks and slowly dissolves with evolution of heat and hydrochloric acid. Acetic acid is left.

3. Treated with alcohols or alcoholates, esters are formed. To a little in a test-tube add an equal volume of alcohol. Then add some brine. A layer of ethyl acetate separates.

4. With aniline it produces white solid acetanilide.

2. **Preparation of an acid anhydride. Acetic anhydride.**

$$CH_3 . CO . ONa + CH_3 . CO . Cl = NaCl + (CH_3 . CO)_2O.$$

Heat about 40 gms. of crystalline sodium acetate in a clean tin dish (sand-tray) till water of crystallisation has all been driven off. Just melt the anhydrous salt and allow it to cool. Powder it finely and place 20 gms. in a distilling flask fitted with tap-funnel and receiver exactly as in the last experiment. From the funnel add slowly 16 gms. of acetyl chloride. When added heat carefully, using a wire gauze and a small flame which is moved about. Distil over all that will come, and redistil with a thermometer and similar condensing arrangement. Collect the fraction between 130° and 140°. Yield, about 16 gms.

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An alternative preparation is to treat 6 molecules of sodium acetate with 1 molecule of $POCl_3$. Redistil from a little sodium acetate.

Properties.—1. Colourless liquid with pungent odour. B.P. 138°; S.G. 1·08 at 15°.

2. It gives similar tests with water and alcohol to those of acetyl chloride, except that no hydrochloric acid is produced.

Note.—By using the salt of one acid and the chloride of another in the above preparation (taking calculated quantities), *mixed* anhydrides are produced.

3. **Esterification of organic acids.**

Preparation of acetic ester.—(i) The esterification of organic acids is carried out directly by treating the alcohol with the required acid, but the action is reversible.

$$CH_3 . CO . OH + C_2H_5 . OH \rightleftharpoons CH_3 . CO . OC_2H_5 + H_2O.$$

To make the action go to the right as far as possible we may

(*a*) Use a dehydrating agent.

(*b*) Use an excess of alcohol.
(*c*) Use an excess of acid.
} (Only where really necessary to esterify the *whole* of an acid or alcohol, as in research work.)

(*a*) *Use of a dehydrating agent.*—(i) Fit a 500 c.c. flask with a tap-funnel and a thermometer (which will be immersed in the liquid in the flask), and attach to a condenser and receiver. Into the flask run a mixture of 50 c.cs. of alcohol and 40 c.cs. of concentrated sulphuric acid. Warm gradually on a sand-bath to 140°, and add, through the tap-funnel, a mixture of 100 c.cs. of alcohol and 100 c.cs. of glacial acetic acid at the same rate as the liquid distils. The distillate will contain, besides the ester, some ether, acetic acid, alcohol, water and sulphur dioxide. Pour into a basin and add sodium carbonate till the acid is neutralised. Remove the upper layer and add to it in a separating funnel a solution of 75 gms. of calcium chloride in 75 c.cs. of water. Shake well; this removes the alcohol. Separate the bottom layer of calcium chloride, and stand the upper layer over solid calcium chloride overnight. Distil on a water-bath and collect the fraction between 75°-80°. Yield, 75-80 gms.

Properties.—1. Colourless liquid; pleasant smell (pear-drops). B.P. 77°; S.G. ·907 at 15°; somewhat soluble in water; miscible with organic solvents.

2. Boiled under a reflux with alkali, the acetate of the metal and ethyl alcohol are formed. Esters are estimated in this manner, using a known volume of standard alkali and titrating the excess.

(ii) A more general dehydrating agent is hydrochloric acid gas. Its exact method of action is uncertain, but it is frequently used where sulphuric acid chars the alcohol or acid.

(*a*) The method employed is to mix the required quantities of acid and alcohol (both anhydrous) in the distilling flask, and pass in dry hydrochloric acid gas to saturation. The liquid is then boiled for some time (reflux) and distilled. Wash and purify as before.

(*b*) In case the whole of the acid is required as ester, excess of alcohol may be dropped or distilled into the boiling mixture whilst the distilla-

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tion is going on, hydrochloric acid gas being passed through at the same time.

Prepare ethyl oxalate (use anhydrous oxalic acid) by method ii. (*b*), and amyl benzoate by method ii. (*a*).

The oxalate is fractionated to separate from water, alcohol, etc. B.P. 181°.

The benzoate is simply poured into water (*not* distilled) after boiling under the reflux, washed with sodium carbonate, dried and distilled. B.P. 256°. Use an *air* condenser.

(*c*) *Fischer and Speier* recommend passing hydrochloric acid gas into the alcohol and acid till the absorption is about 7 %. Then boil with a reflux for an hour. Purify according to the properties of the ester. (Make amyl benzoate thus :)

(iii) The acid chloride is treated with the anhydrous alcohol or with sodium alcoholate, using calculated quantities. This reaction is quantitative. Filter from the ppt. of sodium chloride and fractionate.

Note.—The carbonic esters are prepared by this method.

(iv) *By treating the silver salt of the acid with the alkyl iodide.*—The silver salt is prepared by *exactly* neutralising the acid with ammonia, and adding a slight excess of silver nitrate solution. Filter off the ppt. at the pump, wash with several small amounts of ice-cold water and dry in the dark in a steam-oven or desiccator.

The required amounts of the dried salt and the alkyl iodide are boiled in a small flask with a reflux for about an hour ; it is advantageous to employ a small excess of the iodide.

The liquid is filtered from the silver iodide and the ester purified accordin to its properties.

If *methyl* esters are required, *Werner and Seybold* recommend the action of methyl sulphate on the sodium salt of the acid in water solution, at a temperature of 30°-40°.

Note.—Methyl sulphate vapour is highly poisonous and must not be inhaled.

(v) *Preparation of acid esters.*—These can be universally prepared by the action of the acid anhydride on the *calculated quantity* of sodium ethylate. The sodium salt is thus obtained ; this on treatment with acid and extraction with ether gives the required ester.

Note.—If the acid anhydride is a solid the alcohol may be used instead of sodium ethylate. Normally, excess of alcohol is employed, and the reagents are boiled for half an hour under a reflux.

As an example try a succinate or phthalate.

4. **Preparation of an acid amide.**

(i) *Acetamide,* $CH_3 . CO . NH_2$.—To 60 gms. of glacial acetic acid in a 300 c.cs. distilling flask add solid ammonium carbonate till the mixture is alkaline. Attach an air-condenser and fit the flask with a thermometer. Distil carefully, collecting separately the distillate above 160°. This is melted and redistilled, collecting above 180°. Fractionate this portion again, drain the solid coming over above 200° and crystallise from ether. B.P. 222°.

$$CH_3 . CO . ONH_4 = H_2O + CH_3 . CO . NH_2.$$

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Far better yields are obtained by one of the following modifications :

(*a*) Heat the ammonium acetate in a sealed tube for 5 hours at 200°, as in the Carius method of determining halogens (see p. 417). The contents of the tube are then distilled as above.

(*b*) Heat equal weights of ammonium acetate and glacial acetic acid under a reflux for 4-5 hours. Distil and treat the distillate as before. (Hofmann, *B.* 1882, **15**, 979.)

Properties.—1. White crystalline solid, soluble in water and alcohol. M.P. 82° ; B.P. 222°. Usually smells like mice excrement, but not when quite pure.

2. On boiling with water (or dilute acids or alkalis) it is hydrolysed to ammonium acetate.

3. Boiled with alkali, ammonia is evolved, but *not* when ground with quick-lime (distinction from ammonium salts).

4. Treated with sodium nitrite and dilute acid, nitrogen is evolved.

$$CH_3 . CO . NH_2 + O : N . OH = CH_3 . CO . OH + N_2 + H_2O.$$

5. With bromine and alkali (hypo-bromite) a primary amine is formed on warming. (See preparation of methylamine.)

(ii) A general method for preparing amides consists in treating the acid chloride with concentrated ammonia. It is most suitable when the amide is insoluble, but any amide can be made thus.

The acid chloride is added dropwise to some excess of ·880 ammonia, filtered, washed and dried in the usual way.

$$C_6H_5 . COCl + NH_3 = C_6H_5 . CO . NH_2 + HCl.$$

(iii) Another general method is to treat the ester with excess of ·880 ammonia.

(*a*) **Preparation of oxamide.**—To a little oxalic ester add excess of ·880 ammonia. Set aside for an hour. Filter, wash and dry in the usual way.

$$(CO . OC_2H_5)_2 + 2NH_3 = (CO . NH_2)_2 + 2C_2H_5OH.$$

(*b*) **Preparation of oxamethane.**—Into 50 c.cs. of absolute alcohol pass dry ammonia gas for 10 minutes. Weigh the flask before and after to find the weight of ammonia taken. Calculate the weight of oxalic ester required. Cool both liquids on ice, and slowly add the ammonia to the ester. Filter from any oxamide and set aside to crystallise.

$$(CO . OC_2H_5)_2 + NH_3 = \begin{matrix} CO . OC_2H_5 \\ | \\ CO . NH_2 \end{matrix} + C_2H_5OH.$$

Properties.

Oxamide.—Snow-white micro-crystalline body, decomposing when heated. Almost insoluble in water and alcohol. Boiled with alkalis it is hydrolysed to oxalic acid and ammonia.

Oxamethane.—White prisms, soluble in alcohol. Boiled with alkalis it is hydrolysed to oxalic acid, ammonia and alcohol.

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5. **Preparation of a nitrile from an amide.**—*Acetonitrile from acetamide.*

$$CH_3 . CO . NH_2 - H_2O = CH_3 . CN.$$

Into a small dry retort place as quickly as possible, by means of a paper-funnel and a glass-rod, 20 gms. of phosphoric anhydride. Introduce also about 10 gms. of *dry* powdered acetamide and shake well together. Distil, using a large luminous flame moved constantly about. Shake the distillate with a little water and add solid potassium carbonate till no more will dissolve. The nitrile floats to the top and is separated and redistilled from more phosphoric anhydride. Collect the fraction from 80°-83°.

Properties.—1. Liquid; pleasant odour; B.P. 82°; S.G. 0·79. Somewhat soluble in water, but readily "salted out."

2. Boiled with potash (reflux) or digested and warmed with 50 % sulphuric acid, it is hydrolysed to acetic acid and ammonia, *via* the amide. By standing overnight with cold concentrated hydrochloric acid the amide is formed, and can be extracted with ether.

3. Dissolved in alcohol and reduced with sodium or sodium amalgam, a 1^{ry} amine is produced, which gives the carbamine reaction. (See under Chloroform.)

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CHAPTER VI.

PREPARATIONS FROM SALTS OF THE FATTY ACIDS.

1. **Preparation of the acid.**—*The lower acids* (except formic) may be obtained by distilling the sodium salts with strong sulphuric acid. The anhydrous acid distils.

If the calcium salt is supplied, distil with dilute sulphuric acid, make the sodium salt from the distillate and treat as above.

Formic acid may be made by filling the inner tube of a Liebig condenser with lead formate, held in place by glass-wool plugs. Fit this to a flask in the manner of a reflux condenser. The cork also carries an exit tube. Immerse the flask in cold water, pass steam through the outer jacket of the condenser and pass a current of hydrogen sulphide over the lead formate from top to bottom. Filter if necessary.

The higher acids are for the most part insoluble in water; they are made by adding the salt to hydrochloric acid and filtering or separating.

2. **Preparation of a hydrocarbon.**—Heated with soda-lime, the sodium salts of most fatty acids are decomposed into sodium carbonate, and a paraffin with one C atom less than the acid. The method, however, is used only for methane.

Preparation of methane, CH_4.—Heat an *intimate* mixture of 2 parts of soda-lime and 1 part of anhydrous sodium acetate in a small flask connected to a pneumatic trough. Collect the gas in the usual way and examine its properties.

$$CH_3COONa + NaOH = Na_2CO_3 + CH_4.$$

Properties.—1. Gas, colourless, odourless when pure; B.P. $-164°$.

2. Burns with a non-luminous flame, though as above prepared it contains other hydrocarbons which burn with a luminous flame. These may be removed by fuming sulphuric acid.

3. It reacts with bromine vapour, producing fumes of hydrobromic acid.

4. It does not decolorise Baeyer's reagent (alkaline permanganate).

3. **Preparation of an aldehyd from the corresponding calcium salt and a formate.**

$$\begin{array}{c} CH_3 . CO . OCaO . OC CH_3 \\ + \\ CH . O OCaO OC . H \end{array} = 2CaCO_3 + 2CH_3 . CH : O.$$

Molecular quantities as indicated by the equation are *intimately mixed* (success depends upon this) and dry distilled with a luminous flame from a

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flask connected to a condenser and receiver as for the preparation of aldehyd, *q.v.* The receiver contains ether, which is afterwards treated with ammonia, as in Chapter III.

4. **Preparation of ketones from calcium (barium, etc.) salts.**

$$CH_3 . \boxed{CO . OCaO .} OC . CH_3 = CaCO_3 + (CH_3)_2CO.$$

This method is usually adopted only for acetone. Heat slowly a quantity of anhydrous calcium acetate in a hard glass flask connected to a condenser and well-cooled receiver. The heating is done by a luminous flame kept in motion. The distillate is shaken with water, filtered to remove tarry matter (if necessary) and distilled. The portion of distillate up to 75° is treated with calcium chloride (fused) overnight and re-distilled. Collect between 56° and 60°.

Note.—If no tarry matter be present, fractionate the original distillate at once.

Properties.—1. Liquid; B.P. 56°; S.G. ·797 at 15°. Miscible with water, alcohol and ether.

2. Like alcohol it gives the iodoform test.

3. It can be distinguished from alcohol by Reynold's mercuric oxide test. Add *excess* of potash to a solution of mercuric chloride. Add the acetone. A soluble mercury compound is formed, and hence on filtering mercury will be found in the filtrate. (Hydrogen sulphide test.)

4. It does *not* reduce Fehling's solution nor give the silver-mirror test, nor does it give Schiff's reaction. (Difference from aldehyd.)

5. Like aldehyd it gives a crystalline ppt. with saturated bisulphite solution.

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CHAPTER VII.

HYDROLYSIS OR SAPONIFICATION.

HYDROLYSIS is the process whereby a body is split into two or more compounds with simultaneous fixation of water, which acts as H and OH. It is usually carried out by boiling with acid or alkali. A case already given is the preparation of alcohols from halogen derivatives. The saponification of a fat has also been given in Chapter II.

1. **Hydrolysis of ethyl acetate.**—Put 25 gms. of ethyl acetate into a 250 c.c. flask fitted with a reflux, and add 20 gms. of potash or 15 gms. of caustic soda in 50 c.cs. of water. Boil gently for ¾ hr. (or until the ester has gone into solution). Distil with a thermometer till the temperature reaches 100°.

Treatment of distillate.—Add solid potassium carbonate till no more dissolves. Separate the top layer of "salted out" alcohol, dry and distil over quick-lime.

Treatment of residue.—Just neutralise with dilute sulphuric acid and evaporate dry. Powder the product and distil with strong sulphuric acid. Anhydrous acetic acid distils at 118°.

Similarly any ester can be hydrolysed, and the alcohol and alkali salt of the acid obtained, even if the latter be inorganic. The actual separation of the acid will, of course, vary with the nature of the acid.

Note that ethyl *iso*-cyanate yields ethylamine.

$$\begin{array}{c} C_2H_5N:C:O \\ + \\ H_2O \end{array} = CO_2 + C_2H_5NH_2,$$

which should be absorbed in hydrochloric acid.

2. **Hydrolysis of nitriles.**—All nitriles can be hydrolysed to the corresponding acids by boiling with acids or alkalis.

$$R.CN + H_2O \rightarrow R.CO.NH_2 + H_2O \rightarrow R.CO.ONH_4.$$

The intermediate amide can be obtained by carrying out the hydrolysis with cold concentrated hydrochloric acid, with which the nitrile is allowed to stand till it has gone into solution. The amide can then be ether-extracted. It is *not*, however, a convenient preparation of amides.

(*a*) *Hydrolysis of methyl cyanide* (*aceto-nitrile*).—Boil 10 gms. of the nitrile with 40 gms. of 50 % sulphuric acid for an hour, under a reflux condenser, then distil. Aqueous acetic acid comes over. Purify as already described.

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If the ester is required it may be obtained directly from the nitrile by dissolving in alcohol and saturating with hydrochloric acid gas. (*See malonic ester.*)

(*b*) *Hydrolysis of succino-nitrile.*—This is the last stage in the synthesis of succinic acid. (See p. 308 for nitrile.)

Dissolve 20 gms. of the nitrile in an equal weight of alcohol. Add 20 gms. of potash dissolved in 20 c.cs. of water. Boil (reflux) as long as ammonia is evolved. Cool, render acid with hydrochloric acid, filter and evaporate dry (water-bath). Grind up the product and boil well (under a reflux) with alcohol. Filter from the insoluble potassium chloride, evaporate the filtrate and recrystallise from water.

Properties of succinic acid.—1. Colourless crystals. M.P. 180°, B.P. 235°, when water is given off and the anhydride formed.

2. Ferric chloride added to the *neutral* solution gives a brown ppt. of basic ferric succinate (used to separate iron from manganese).

3. **Hydrolysis of glucosides.**—These are naturally occurring condensation products of glucose with various organic bodies.

The hydrolysis is effected by boiling the glucoside with 10% caustic alkali or mineral acid under a reflux. The products may be separated and identified according to their nature (*e.g.* distillation in steam, precipitation, etc.).

The best-known glucosides are as follows:

Amygdalin, $C_{20}H_{22}NO_{11}$. M.P. 200°. Occurs in bitter almonds. Hydrolysis products.—Glucose, benzaldehyde, hydrocyanic acid. (Liebig and Wohler, *Ann. Chim. Phys.*, **64**, 185.)

Salicin, $C_{13}H_{18}O_7$. M.P. 196°. Soluble in hot water. Conc. H_2SO_4 gives a blood-red colouration.

Hydrolysis products.—Glucose, *o*-hydroxy-benzyl alcohol (salicylic alcohol). This alcohol in neutral solution gives a deep blue coloration with ferric chloride.

Note.—If conc. KOH is used for the hydrolysis, a salt of salicylic acid is produced. (See p. 385.)

Indican (not to be confused with urinary indican (pp. 299, 395)). This occurs in wood and in the indigo plant.

Hydrolysis products.—Glucose, indigo. (See p. 394.)

Arbutin, $C_{12}H_{16}O_7$. M.P. 157°.

Hydrolysis products.—Glucose, hydroquinone.

Ferric chloride gives a blue colouration to the solution in water.

See also Fischer (*B.* **28**, 1151) for the preparation of α-methyl glucoside. M. P. 165°. β-methyl glucoside. M.P. 107°.

Hydrolysis products.—Glucose, methyl alcohol.

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CHAPTER VIII.

AMINES.

1. **Preparation of a primary amine from an amide.** (Hofmann, *B.* **14**, 2725; **15**, 451, 762.)—This is a general reaction and useful theoretically, as it affords a method of eliminating a carbon atom and so of descending an homologous series.

(1) $CH_3CONH_2 + Br_2 = CH_3CONHBr + HBr$.

(2) $CH_3CONHBr - HBr = CH_3N : C : O$ (not isolated).

(3) $CH_3N : C : O + H_2O = CH_3NH_2 + CO_2$.

To 15 gms. of acetamide add slowly 40 gms. (13·5 c.cs.) of bromine, followed by 10 % caustic soda solution, until the colour changes to a pale yellow. The flask is cooled under the tap during this operation.

Fit a distilling flask with tap-funnel and condenser, with adapter fixed to receiver. Run 75 c.cs. of 50 % caustic soda into the flask, warm to 65°, and slowly run in the above mixture without allowing the temperature to rise. The yellow colour disappears. Replace the tap-funnel by a tube leading from a steam boiler and distil in a rapid current of steam, absorbing the distillate in 100 c.cs. of dilute (1 : 4) hydrochloric acid which has been placed in the receiver. The adapter, which must be fitted to the receiver with a cork, should only just touch the surface of the acid in the receiver. Continue the distillation till the distillate is no longer alkaline. Evaporate the acid solution dry, finally on a water-bath. A mixture of methylamine hydrochloride and ammonium chloride is obtained. Powder and digest repeatedly with absolute alcohol (or, better, exhaust with absolute alcohol in a Soxhlet apparatus). The amine salt may be crystallised from the solution.

The course of this reaction illustrates the Beckmann transformation; the mono-bromamide existing also in the "enolic" form.

$$\begin{array}{ccc} CH_3C=O & \longrightarrow & CH_3C-OH \\ \quad\;\; | & & \quad\;\; \| \\ \quad NHBr & \longleftarrow & \quad BrN. \end{array}$$

In this the Beckmann transformation occurs, the bromine and methyl group changing places.

$$\begin{array}{ccc} CH_3 . C-OH & & Br . C-OH \\ \quad\;\; \| & \longrightarrow & \quad\;\; \| \\ \quad BrN & & \quad CH_3 \cdot N. \end{array}$$

This loses HBr, giving an isocyanate, which is hydrolysed in the usual manner.

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All the intermediate products have been isolated (though not necessarily with any one given amide), and the reaction has been followed in all its stages.

The free base may be liberated from the hydrochloride by warming with alkali. It is a gas which burns and possesses an odour similar to that of ammonia, but somewhat "fishy." It is strongly alkaline, and its solution in water resembles ammonia solution in its properties.

Treated with nitrous acid (nitrite followed by acid) *all* 1ry amines on warming evolve nitrogen and leave the corresponding alcohol. (*Important reaction.*)

2. **Preparation of an amine by Mendius' reaction.**—Reduction of nitrile (oxime or hydrazone).

Ethylamine from aceto-nitrile (or acetoxime).—In a round-bottomed flask place 15 gms. of sodium. Fit a small reflux, to the top of which, to prevent loss of the amine, fit a U-tube containing glass-wool moistened with hydrochloric acid (1 : 1). Pour into the flask 7 gms. of aceto-nitrile (or 7·5 of acetaldoxime dissolved in 45 c.cs. of absolute alcohol). Immediately attach the reflux and boil gently. If a crust forms on the surface add more alcohol. When the sodium has dissolved, allow to cool, add 40 c.cs. of water and distil into hydrochloric acid as in the previous preparation (No. 1). Collect as the hydrochloride by evaporation. The free base is obtained in a similar manner to that in which methylamine is obtained, and has very similar properties.

Note.—A given cyanide gives the next higher amine. *E.g.* methyl cyanide gives ethylamine.

3. **Reduction of hydrazones.** (Tafel, *B.* **22**, 1855).—This is best done in acetic acid solution. Dissolve 8 gms. of acetone hydrazone in 150 c.cs. of alcohol, and to this, with constant cooling, add acetic acid and 3 % sodium amalgam, small quantities at a time. Keep the acetic acid in excess to prevent loss of amine and continue till about twice the theoretical quantity of sodium has been added. Digest with a reflux for 1½ hours on a water-bath. Separate the mercury and pptd. sodium acetate, render strongly alkaline with caustic soda, and distil. The aniline is readily separated as it boils at 182°.

B.P. of 2ry propyl 1ry amine; 31·5° at 743 mm.

4. **Gabriel's Phthalimide reaction.** (*B.* **20**, 2224; **21**, 566, 2669.)—The method consists in heating the alkyl halide with potassium phthalimide and saponifying the product.

(*a*) *Preparation of phthalimide.*—Phthalic anhydride is heated to 130° in a flask and dry ammonia led in for an hour. The temperature is gradually increased to about 230° (oil or fusible metal bath). Crystallise the product from ether.

Properties.—White needle-like crystals. M.P. 233°.

(*b*) *Preparation of the potassium salt.*—Dissolve the required quantity of phthalimide in alcohol, and add the calculated quantity of potash dissolved in alcohol. Filter, wash with alcohol and ether and dry.

Properties.—White crystalline salt, sparingly soluble in the usual solvents.

(*c*) *Preparation of the amine.*—The calculated quantities of alkyl iodide (bromide, etc.) and potassium phthalimide are heated in a sealed tube to 150°-200°. The product is crystallised from ether to remove potassium

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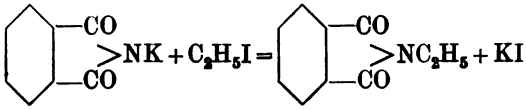
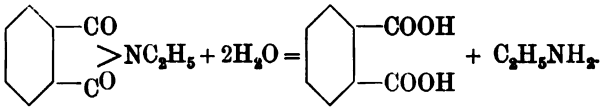
halide, and heated in a sealed tube to 200° with 3 parts of fuming hydrochloric acid. Obtain the free base as before.

Reactions:



$$C_6H_4\begin{matrix}-CO\\-CO\end{matrix}>NK + C_2H_5I = C_6H_4\begin{matrix}-CO\\-CO\end{matrix}>NC_2H_5 + KI$$



$$C_6H_4\begin{matrix}-CO\\-CO\end{matrix}>NC_2H_5 + 2H_2O = C_6H_4\begin{matrix}-COOH\\-COOH\end{matrix} + C_2H_5NH_2.$$

5. **Preparation of a quaternary base from its iodide.**—The solution of the salt is digested and warmed with excess of moist freshly-pptd. lead hydroxide or silver oxide. Boil, cool, filter off the pptd. halide, and evaporate in a silver or nickel basin.

Properties.—The quaternary bases are white, crystalline, hygroscopic substances which closely resemble caustic potash in both physical and chemical properties.

6. **Distinction between primary, secondary and tertiary amines.**—1. A primary amine gives the carbamine reaction with chloroform and alcoholic potash. Secondary and tertiary amines do not.

2. Nitrous acid is the best reagent to distinguish between them.

(*a*) To the acid solution of the amine salt add sodium nitrite solution. Warm. A brisk effervescence due to nitrogen = primary amine.

$$C_2H_5{}^{\bullet}NH_2 + O : N . OH = C_2H_5{}^{\bullet}OH + N_2 + H_2O.$$

(*b*) If a yellow oil separates (nitrosamine), the amine is secondary.

$$(CH_3)_2 : NH + HO . N : O = (CH_3)_2 : N . N : O + H_2O.$$

Extract with ether, wash with water and evaporate off the ether. Warm the residue with phenol and strong sulphuric acid, dilute by pouring into water and render alkaline with caustic soda. A deep blue colour is produced.

(*c*) Tertiary amines do not react at all with nitrous acid.

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CHAPTER IX.

CYANOGEN DERIVATIVES.

THE starting-point of many of these is potassium ferro-cyanide.

1. **Preparation of potassium cyanide** (highly poisonous).—Potassium ferro-cyanide is fused with potassium carbonate.

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2.$$

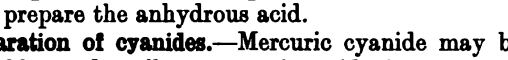
Extract the powdered mass with alcohol, which removes the cyanate. Extract the cyanide with water, filter and evaporate (draught-cupboard).

2. **Preparation of hydrocyanic acid.**—Distil a mixture of 100 gms. of potassium ferrocyanide (powdered), 70 gms. of strong sulphuric acid, and 140 c.cs. of water from a flask fitted with a condenser, fitted air-tight to the bottle in which the specimen is to be kept. Another tube leads from the bottle and dips into cold water. The whole operation must be conducted in an *efficient* draught-cupboard, and the greatest care taken not to inhale any of the vapours. Pour the aqueous solution into the bottle and do not attempt to prepare the anhydrous acid.

3. **Preparation of cyanides.**—Mercuric cyanide may be obtained by dissolving freshly-pptd. yellow mercuric oxide in aqueous hydrocyanic acid. Filter from excess of oxide and evaporate to crystallisation, occasionally adding fresh hydrocyanic acid solution as the smell disappears.

Silver cyanide is made by double decomposition in the usual way.

4. **Preparation of cyanogen.**—Heat mercuric cyanide in a test-tube. When the gas is evolved, light it at the mouth of the tube and note the characteristic flame.



$$Hg(CN)_2 = C_2N_2 + Hg.$$

5. **Preparation of potassium cyanate, KCNO** (for urea).

(*a*) *From potassium ferrocyanide.*—Gently heat 50 gms. of the salt on a clean sand-tray till the water of crystallisation has been driven off. Grind up and heat again at 110° to make sure that it is quite dry. Grind it up, whilst still warm, with 35 gms. of potassium dichromate, and heat in a shallow iron pan till it has charred and begins to fuse. Cool, grind up and boil for 10 minutes with 100 c.cs. of 80 % alcohol (reflux). Decant the solution from the residue and repeat twice more with similar quantities of alcohol. Evaporate the combined extracts to dryness on the water-bath. Use at once for the preparation of urea (*q.v.* p. 336).

(*b*) *From potassium cyanide.*—Fuse 1 part of potassium cyanide with 2 parts of red lead in a clean sand-tray. Cool and extract as before.

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6. **Preparation of thio-cyanates.**—(See Book I., preparations 165 and 166.)

7. **Preparation of sodium nitro-prusside, $Na_2FeNO(CN)_5$, $2H_2O$.**

$$K_4Fe(CN)_6 + 2HNO_3 = K_3Fe(CN)_6 + KNO_3 + NO_2 + H_2O.$$
$$2K_3Fe(CN)_6 + 2NO_2 = 2K_2Fe(CN)_5NO + 2KCN + O_2.$$

The free acid formed is then neutralised with soda.

To 60 gms. of finely-powdered ferro-cyanide add 60 gms. of strong nitric acid diluted with its own volume of water. Shake thoroughly, and warm on a sand-bath until a test portion no longer reacts with ferrous sulphate (no ferricyanide left). Cool and filter, concentrate the filtrate somewhat, and again filter from potassium nitrate. Make alkaline with caustic soda and allow to cool. Filter again on the pump, washing the residue with 50 % alcohol and adding the washings to the filtrate. Now evaporate dry, and extract with 80 % alcohol (best in a Soxhlet apparatus). The potassium nitrate will now be left, and the nitro-prusside is obtained on evaporating the alcoholic solution after addition of some water.

Properties.—1. Ruby red crystals.

2. Gives a purple colour with alkaline sulphides, for which it is used as a test.

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CHAPTER X.

SUBSTITUTED ACIDS AND THEIR DERIVATIVES.

Chlorination of a fatty acid.

1. **Preparation of chloracetic acid.**—Weigh out 40 gms. of glacial acetic acid in a tubulated retort, fix the retort with its neck sloping upwards and attach a reflux condenser. A tube from the end of this, terminating in an inverted funnel dipping into a beaker of strong caustic soda, serves to absorb excess of chlorine. (See Fig. 98.) To the contents of the retort add 4 gms.

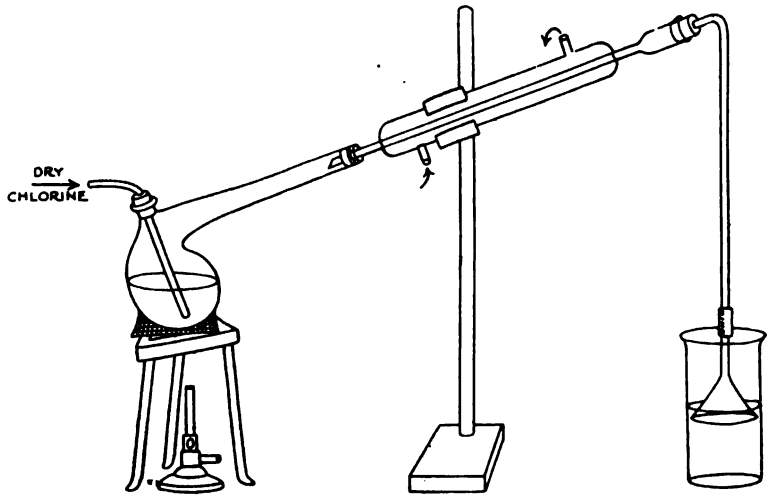

FIG. 98.

of sulphur and weigh the whole. Now pass a rapid current of chlorine through a tube fixed in the tubulus of the retort, the acid being boiled all the time and the apparatus placed in sunlight if possible. When there is an increase in weight of 15-16 gms. in the contents of the retort (about 12 hours), transfer to a distillation flask fitted with a thermometer and distil. Reject the portion distilling below 160° and collect the fraction 160°-190°. Drain this (it will nearly all solidify in the receiver) and distil the solid portion again. B.P. 186°.

Properties.—1. Colourless crystals. M.P. 63°. Soluble in water. Smell like acetic acid.

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2. Solution does not give a ppt. with silver nitrate.

3. Heated on oxidised copper gauze it gives a fine blue-green flame. (Beilstein's test for halogens.)

4. With ferric chloride, amyl alcohol, etc., it reacts very similarly to acetic acid.

2. **Preparation of dichloracetic acid.**—Carry on the above preparation until the increase in weight is 30 gms. Distil, collect the fraction 170°-200°, and redistil this. B.P. 190°-191°; M.P. −4°.

3. **Preparation of trichloracetic acid.**—The continued chlorination of acetic acid may be used, but is very tedious. It is more convenient to oxidise chloral.

In an open dish melt 50 gms. of chloral hydrate and carefully add 20 gms. of nitric acid of S.G. 1·52. Transfer to a retort and distil. Treat the distillate above 175° as for monochloracetic. B.P. 195°-200°.

Properties.—1. Colourless deliquescent crystals. M.P. 52°.

2. Hydrolysis with alkalis yields chloroform.

3. In other respects closely resembles acetic acid.

Bromine substituted acids by the Hell-Volhard-Zelinsky reaction.—Hell, *B.* **14**, 891; Volhard, *A.* **242**, 144; Zelinsky, *B.* **20**, 2026.

4. **Preparation of bromacetic acid.**—To 25 gms. of perfectly dry glacial acetic acid in a tubulated retort add 5 gms. of red phosphorus which has been washed with water and dried in a steam oven. Slope the neck of the retort upwards and connect it to a reflux and an absorption vessel as for chloracetic acid. The latter contains water to absorb hydrobromic acid. Fit a tap-funnel into the tubulus of the retort and slowly run in (with cooling at first), 100 gms. (34 c.cs.) of bromine. Then boil till the colour of the bromine has gone. Distil the residue under diminished pressure (50-60 mm.) and collect the fraction between 50°-55°. The bromacetyl bromide obtained is added to hot water in the draught-cupboard, and the bromacetic acid obtained is fractionated under diminished pressure. Redistil at ordinary pressure, using an air-condenser, and collect the portion boiling above 170°.

Alternatively, the bromacetyl bromide may be treated with the calculated quantity of water and the resulting crystalline mass fractionated.

Properties.—1. Colourless crystals. M.P. 50°; B.P. 208.°

2. Otherwise closely resembles chloracetic acid.

Bromo-succinic acid may be similarly made; the bromo-succinyl bromide is added to 2½ times its volume of boiling water and the acid extracted with ether after cooling.

5. **Preparation of amino-acids.**

(i) *Glycocoll*, $CH_2 . NH_2 . COOH$, *from chloracetic acid.*—Into a litre flask put 50 gms. of chloracetic acid dissolved in 50 c.cs. of water, and add 600 c.cs. of 26 % ammonia (S.G. ·905). Stir thoroughly and leave for 24 hours. Remove ammonia in excess by warming and drawing a current of air through the liquid by means of a filter-pump. Boil the liquid and add copper carbonate till no more will dissolve. Filter and crystallise the copper glycocollate by evaporating till ready to crystallise, adding an equal volume of alcohol and setting aside for 24 hours. Wash with (*a*) 60 % alcohol, (*b*) 90 % alcohol till the washings are colourless.

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Dissolve in the minimum of water, add a little freshly-pptd. aluminium hydroxide, and saturate with hydrogen sulphide. Filter, wash the ppt. with hydrogen sulphide water and add the washings to the filtrate. Evaporate to crystallisation. Sometimes called Glycine. (See p. 298.)

Properties.—Colourless crystals, readily soluble in water, melting at 236° with complete decomposition.

Alanine, α-chloro-propionic acid, may be made similarly, but its preparation will illustrate another method.

(ii) *Alanine from acetaldehyd* (Strecker's synthesis).

$$CH_3.CHO + NH_3 = CH_3.CH\begin{cases}OH\\NH_2\end{cases} + HCN = CH^3.CH\begin{cases}NH_2,\\CN\end{cases}$$

which on hydrolysis $\longrightarrow$ $CH_3CH\begin{cases}NH_2\\COOH.\end{cases}$

In a flask fitted with a reflux boil a mixture of 2 parts of aldehyd-ammonia, 3 parts of potassium cyanide and excess of hydrochloric acid, in aqueous solution, for several hours. Disconnect, evaporate and ppt. the ammonium chloride by addition of alcohol. Filter. The filtrate will contain alanine hydrochloride. Dissolve it in water and add excess of freshly pptd. lead hydroxide (or silver oxide). Filter; pass hydrogen sulphide through the filtrate if lead hydroxide is used, filter from the lead sulphide, and evaporate to crystallisation.

Properties.—1. Hard needle-shaped crystals, soluble in 5 parts of water. Easily soluble in hot water or alcohol.

2. Sublimes if heated gently, but if rapidly heated it decomposes into ethylamine and carbon dioxide.

6. Preparation of an oxy-acid. Lactic acid.

(*a*) *From alanine.*—Dissolve 20 gms. of alanine in 100 gms. of warm water. Add a solution of sodium or potassium nitrite (rather more than the calculated quantity). Then gradually add dilute sulphuric acid till in excess. Warm till no more nitrogen is evolved. Cool, extract with ether and allow the ether to evaporate.

(*b*) *From aldehyd, by hydrolysis of the cyanhydrin.*—Dissolve the aldehyd in ether and add the calculated quantity of finely-powdered pure potassium cyanide. Add to this, a little at a time, concentrated hydrochloric acid, till excess has been added. Leave for 2 hours, decant the ethereal solution and distil off the ether. The cyanhydrin left is boiled under a reflux with concentrated hydrochloric acid for an hour. Neutralise with chalk, evaporate dry, add a slight excess of dilute sulphuric acid to the residue, and extract with ether. Evaporate the ether and the lactic acid is left as a thick, sour liquid.

Properties.—1. Soluble in water, alcohol and ether. M.P. 18°, but is difficult to obtain in crystals.

2. Its solution evaporated in a desiccator deposits crystals of lactic anhydride.

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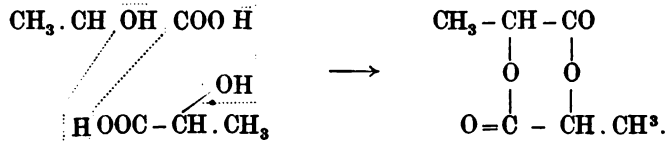
3. Heated to 130° with dilute sulphuric acid, it is decomposed into aldehyd and formic acid.

4. Heated alone it forms lactide (150° in a current of dry air), which is an ester anhydride.



5. With ferric chloride in neutral solution it gives a yellow colour.

As synthesised, lactic acid is not optically active (p. 488), being a racemic mixture of the two active isomers.

Separation of racemic mixtures into active components.

1. *Pasteur's mechanical method.*—(Pasteur, *Ann. Chim. Phys.*, 1848 (3), **24**, 442, 1850 (3), **28**, 56.) This is of great historic interest.

Prepare sodium ammonium racemate, $NaNH_4C_4H_4O_6$, from racemic tartaric acid, crystallise so that a large number of small separate crystals are produced and pick out several at random. Redissolve the remainder and grow the picked ones till large enough to see the secondary facets. Then prepare the acids *via* the calcium salt. (See p. 297, also p. 488, for the constants of tartaric acid, also Gernez, *C. R.* **63**, 843.)

2. *The biochemical method.*—One active component is destroyed by bacteriological means, leaving the other. The racemic body, after sterilisation and the addition of inorganic salts as a culture medium, is infected with a culture on a platinum wire and set in a warm place for several weeks. The remaining active body is separated by physical means.

For examples see mandelic acid (p. 383) and tartaric acid (p. 488), also *B.* **16**, 2720, for the biochemical separation of lactic acid by means of *penicillium glaucum*.

3. *The use of optically active bases.*—Salts of the two forms of an active acid with an active base may have different solubilities.

Purdie and Walker (*J.C.S.* 1892, 754) resolve lactic acid by dissolving 460 gm. strychnine in just enough lactic acid for solution.

Fractionally crystallise eight to ten times, dissolve in water, ppt. strychnine with NH_4OH, filter, evaporate filtrate, and repeat the pptn. with NH_4OH.

The product is *d*-ammonium lactate from which the free acid is obtained by boiling with *Z*nO and crystallising the zinc salt (the first crop contains some *l*-salt), after which H_2S and ethering out yield the acid.

This experiment gives small yields and is very tedious.

They also treat a solution of *i*-lactic acid with sufficient *l*-strychnine to neutralise half of it. The crystals are *l*-strychnine-*l*-lactate, while the liquor contains the free acid, though both are impure.

See also Hirsch (*B.* **27**, 887) for the resolution of cinnamic acid di-bromide with *l*-brucine in alcohol for the *d*-acid, and cinchonidine in benzene for the *l*-acid. The salts are decomposed by mineral acids.

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CHAPTER XI.

DERIVATIVES OF POLYBASIC ACIDS.

A. CARBONIC ACID DERIVATIVES.

1. **Preparation of carbonic ester.**—(*a*) Boil ethyl iodide with some excess of silver carbonate, under a reflux, for 15 minutes. Filter and fractionate, collecting the portion distilling at 124°-128°. B.P. 126°.

(*b*) If phosgene is available, pass it into a solution of sodium in alcohol (sodium ethylate) till no more ppt. of sodium chloride forms. Filter and distil as above.

2. **Preparation of potassium ethyl carbonate.**—Through a clear saturated solution of potash in alcohol pass a current of carbon dioxide, using a funnel as delivery tube to prevent stoppage by the deposited crystals. When no more form, separate and dry on a porous plate.

For **ammonium carbamate** see Book I. p. 72.

3. **Preparation of urea (carbamide), $CO(NH_2)_2$.**—Dissolve 1 part of potassium cyanate in 5 parts of water, and add 1·25 parts of ammonium sulphate. Evaporate to dryness (finally on water-bath) and extract the finely-powdered product with several portions of alcohol by boiling in a flask with a reflux, or, better, in a Soxhlet apparatus. Evaporate the extract to crystallisation on a water-bath. Yield, about half the weight of cyanate taken.

$$NH_4CNO \rightleftharpoons CO(NH_2)_2.$$

Properties.—1. Colourless prisms, soluble in water and alcohol, but not ether. M.P. 132°.

2. Heated gently, ammonia is evolved and the molten mass solidifies to biuret, $NH_2 . CO . NH . CO . NH_2$, which, dissolved in caustic soda and treated with 2 drops of copper sulphate, gives a fine violet colour of copper biuret.

3. Boiled with caustic alkali, ammonia is evolved.

4. Treated with a solution of sodium nitrite and then dilute acid, a copious evolution of nitrogen and carbon dioxide takes place.

$$CO(NH_2)_2 + 2HNO_2 = 3H_2O + 2N_2 + CO_2.$$

5. Treated with alkaline hypobromite or bleaching powder solution, nitrogen is evolved.

$$CO(NH_2)_2 + 3NaOBr + 2NaOH = 3NaBr + N_2 + 3H_2O + Na_2CO_3.$$

(See under Gas analysis.)

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6. A concentrated solution of urea treated with oxalic acid solution gives a white ppt. of urea oxalate, which on recrystallisation from hot water gives beautiful feathery crystals.

7. Concentrated nitric acid added to a strong solution of urea ppts. urea nitrate.

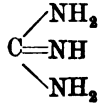
4. **Preparation of thio-urea (thio-carbamide), $CS(NH_2)_2$.**—In a small flask put 40 gms. of ammonium thio-cyanate. Immerse a thermometer in it and melt it by heating in an oil or fusible metal bath. Raise the temperature to 170°-175° and maintain it for an hour. Allow to cool and boil the residue with 60 c.cs. of water. Filter whilst hot. On cooling thio-urea crystallises. Recrystallise from hot water.

$$NH_4CNS = CS(NH_2)_2.$$

Properties.—1. Colourless flat needles. M.P. 172°. Soluble in water and alcohol, not in ether.

2. In many other respects it closely resembles urea.

5. **Preparation of guanidine.**



When ammonium thio-cyanate is heated to a higher temperature we get guanidine thio-cyanate instead of thio-urea. 40-50 gms. of ammonium thio-cyanate are heated for 20 hours to 180°-190° in a retort with a thermometer passing through the tubulus. (Oil-bath.)

The mass is allowed to cool, extracted with boiling water and decolorised by boiling the extract with animal charcoal and filtering. Crystallise the filtrate and recrystallise from alcohol.

To obtain the free base from the thio-cyanate, dissolve 100 parts of the product in the minimum of water and add 58 parts of potassium carbonate and 200 parts of boiling alcohol. The guanidine carbonate thus obtained is decomposed by cold baryta solution (calculated quantity) and the filtered solution crystallised.

Properties.—1. A deliquescent crystalline body. M.P. not very definite.

2. It is strongly alkaline, resembling caustic soda, and absorbs carbon dioxide from the air.

3. Boiled with alkalis, it is hydrolysed first to urea and ammonia, then to carbonic acid and ammonia.

B. DICARBOXYLIC ACIDS AND DERIVATIVES.

1. **Oxalic acid.**—(See Chapter III. Part I.)

Properties.—1. Colourless crystals containing 2 molecules of water of crystallisation. M.P. 100° with evolution of water, and some decomposition to carbon dioxide and formic acid.

2. Heated with strong sulphuric acid, carbon monoxide and dioxide are evolved.

3. Decolorises permanganate in sulphuric acid solution at 60° in a characteristic manner, slowly at first, then more rapidly, with evolution of carbon dioxide.

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4. Neutralised with ammonia and treated with calcium chloride, calcium oxalate is pptd., insoluble in acetic acid.

2. **Oxalic ester, oxamide and oxamethane** have been described in Chapter V.

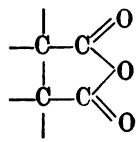
3. **Preparation of malonic ester** (Claisen, *A.* **218**, 131).—This substance is of great importance for many syntheses (see later). Neutralise a solution of 100 gms. of chloracetic acid in 200 gms. of water with 75 gms. of potassium carbonate. Now add 80 gms. of pulverised potassium cyanide, and warm till the reaction starts (draught-cupboard). Then evaporate with vigorous stirring till a thermometer placed in the mass registers 135°. Cool with constant stirring, add $\frac{2}{3}$ the volume of alcohol, saturate with hydrochloric acid gas in a flask fitted with a reflux and heat for 2 hours on a water-bath. Cool, add some ice and extract with ether after first filtering off the pptd. salt. The ether extract is treated in the separation funnel with dilute sodium carbonate solution till it is no longer acid. It is then dried with anhydrous sodium sulphate, the ether distilled off and the residue distilled. B.P. 195°. Yield, 80 gms.

The free acid is obtained by adding twice the volume of strong hydrochloric acid to the cyanacetic acid made as above, then saturating with hydrochloric acid gas and removing the ppt. of potassium and ammonium chlorides after standing overnight. Extract the acid with ether. (Bourgoin, *B.* **33**, 570.)

4. **Preparation of succinic anhydride** (Volhard's method).—Into a 250 c.cs. flask put 75 gms. of succinic acid which has been dried at 100°. Add 110 gms. of acetyl chloride and boil for 2 hours with a reflux. When no more hydrochloric acid gas comes off, distil, using an air-condenser. When the distillate solidifies on cooling, collect the anhydride.

Properties.—1. Crystalline solid. M.P. 120°; B.P. 256°.

2. Heated in a test-tube with a little resorcinol and zinc chloride a red melt is obtained, which when dissolved in caustic soda and poured into water shows a fine green fluorescence. This is characteristic of anhydrides, containing the grouping



C. OXY POLYBASIC ACIDS AND DERIVATIVES.

1. **Tartaric acid** (see pp. 297, 335, 488), $(CHOH)_2(COOH)_2$.

Properties.—1. White crystals, soluble in water. A strong solution treated with a little potash deposits cream of tartar, $KH(C_4H_4O_6)$.

2. On heating the acid (or a salt) it chars and gives off a smell of burnt sugar.

3. Heated with strong sulphuric acid it chars readily (difference from citric acid), and evolves CO, CO_2 and SO_2.

4. Treated with hydrogen peroxide, a little ferrous sulphate, and then excess of alkali, a deep violet colour is produced, caused by the formation of dioxytartaric acid (Fenton's reaction).

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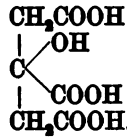
5. Calcium chloride added to a neutral tartrate gives a white ppt. of calcium tartrate in the cold (difference from citric acid).

6. Neutral tartrates give the silver mirror test (see under Aldehyd).

2. **Citric acid.**



(See Chapter III.).

Properties.—1. White crystals. Soluble in water.

2. When it (or a salt) is heated it chars, giving off irritating odours (see next preparation).

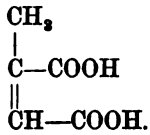
3. Heated with strong sulphuric it behaves like tartaric acid, but not as quickly.

4. Calcium chloride added to a neutral citrate gives no ppt. in the cold, but on boiling, calcium citrate is deposited (distinction from tartaric).

5. It gives no silver mirror test, though ammoniacal silver nitrate is reduced.

6. Silver nitrate ppts. white silver citrate from neutral solutions.

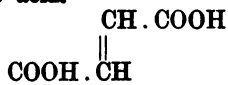
3. **Preparation of Citraconic acid.**



Dry 80 gms. of citric acid at 100° and distil it from a flask or retort connected with an air-condenser. The receiver is a distilling flask (corked to the condenser) the side tube of which leads to the fume-cupboard. Distil rapidly and stop when the distillate becomes brown. Fractionate the distillate and collect the citraconic anhydride between 210° and 220°.

Properties.—Like succinic and phthalic acids it gives a fluorescëin with resorcinol owing to the presence of the characteristic grouping.

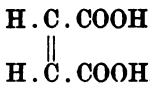
4. **Preparation of fumaric acid.**



(Lassaigne: *Ann. Chim.* [2], 1193).

Heat malic acid to 150° in a flask in an oil-bath. Allow to cool and filter off the fumaric acid. A further crop is obtained on evaporation. It sublimes at 200° without melting.

5. **Preparation of maleïc acid.**



Distil malic or fumaric acid, heating quickly to 200°.

Prisms. M.P. 130°. Soluble in 2 parts of water. It is a geometrical isomer of fumaric acid.

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CHAPTER XII.

DERIVATIVES OF, AND PREPARATIONS FROM GLYCEROL.

Glycerol or Glycerin.—(See Chapter III., Introduction.)

Properties.—1. Thick, sweet syrup.

2. Boils at 290° with decomposition and evolution of irritating vapours (acrolein).

3. A borax bead moistened with glycerol gives a green colour to the bunsen flame.

1. **Preparation of formic acid** (Berthelot, *Ann. Ch. Ph.* (3), **46**, 477).—When oxalic acid is heated with glycerin, carbon dioxide is evolved and formic acid produced. This with glycerin forms an ester, glycerin monoformin, which is hydrolysed by the water of crystallisation in more oxalic acid.

Dry 50 gms. of glycerin by careful heating in an open dish to 170°. Cool and put into a retort fitted with a thermometer, condenser and receiver. Add 50 gms. of crystallised oxalic acid. With the thermometer dipping into the liquid, maintain the temperature at about 105° till the evolution of carbon dioxide slackens. A weak solution of formic acid collects in the receiver. Allow to cool somewhat, add another 50 gms. of oxalic acid and heat up again. This may be repeated with two more portions of oxalic acid, when the distillate will be 55 % formic acid. It is neutralised whilst hot with lead carbonate, filtered, and the lead salt crystallised out and dried. The anhydrous acid is obtained as described in Chapter VI.

Properties.—1. Pungent smelling liquid. M.P. 8°; B.P. 101°.

2. Heated with strong sulphuric acid evolves carbon monoxide without charring.

3. The acid and its salts are strong reducing agents: ammoniacal silver oxide gives a *ppt.* of metallic silver; Fehling's solution is also reduced.

4. With ferric chloride, and with alcohol and sulphuric acid, formates give similar reactions to those of acetates.

2. **Preparation of allyl alcohol, $CH_2:CH.CH_2OH$.**—Into a retort put a mixture of 4 parts of glycerol and 1 part of crystallised oxalic acid, and add a small quantity of ammonium oxalate (0·5 %). Fit with a thermometer and condenser and heat slowly up to 260°. Some formic acid distils at first, and at 200° the receiver is changed. The portion distilling from 200°-260° is redistilled until a portion gives no oily droplets on addition of potassium carbonate. The product is treated with potassium carbonate to salt out the alcohol.

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A further yield may be obtained by treating the residue in the retort with another lot of oxalic acid and repeating the process.

Finally the united products are treated with solid potash and redistilled. B.P. 96°-97°.

Properties.—1. Colourless liquid, penetrating odour. Solidifies at 50° when pure. S.G. 0·858 at 0°. Miscible with water, etc.

2. Oxidation with chromic acid gives the characteristic smell of acrolein.

3. It decolorises bromine water and alkaline permanganate.

3. **Preparation of allyl iodide, $CH_2 : CH . CH_2I$.**—In a tubulated retort mix 13 parts of glycerol and 9 of iodine. Add gradually 3 parts of red phosphorus and shake well till mixed. Distil slowly, keeping the mixture just frothing, otherwise much 2ry propyl iodide is formed. Wash the distillate with dilute caustic soda, water, and finally dehydrate over calcium chloride and rectify. The fraction between 98°-103° is nearly pure allyl iodide. (If coloured with iodine distil from a little red phosphorus.)

Properties.—Colourless liquid, disagreeable odour. B.P. 101°; S.G. 1·79 at 15°.

4. **Secondary propyl iodide, $CH_3 . CHI . CH_3$,** is obtained in the above preparation if the distillation is carried out quickly. A better yield is obtained by using double the quantity of iodine, and yellow phosphorus instead of red. The fraction 85°-90° is redistilled as for allyl iodide.

5. **Preparation of acrolein, $CH_2 : CH . CH : O$.**—In a retort mix 5 parts of anhydrous glycerol with 10 parts of potassium bisulphate (dry) and 4 parts of potassium sulphate. Leave for 12 hours, then distil, gently at first. The receiver, which should be *attached* to the condenser, is cooled with ice. The distillation will take 4-5 hours and the distillate separates into 2 layers. Distil each layer separately, collecting the product below 60°. Redistil from litharge, dry over calcium chloride and redistil. Yield, 40 % of theory.

Properties.—1. Liquid of penetrating unpleasant odour. B.P. 52°. Soluble in 2-3 parts of water.

2. It possesses all the properties both of an aldehyd and of an unsaturated body.

6. **Preparation of glyceric acid, $CH_2OH . CHOH . COOH$** (Debus, *A.* **106**, 79 (1858)).—In a glass cylinder place equal volumes of nitric acid (S.G. 1·5) and of a mixture of equal volumes of glycerol and water, so that they do not mix but form two layers. Leave for 6 days. Evaporate to a syrup, dissolve in water to a dilute solution and neutralise with litharge. Set aside with the excess of litharge for a day, heat on the water-bath for 2 hours and filter hot. Purify the lead salt by crystallisation and decompose it in hot water suspension by saturating with hydrogen sulphide. Filter and evaporate to a syrup. Yield, about 30 % of theory.

Properties.—Thick syrup, soluble in water and alcohol, not in ether.

7. **Preparation of glycerose, $C_6H_{12}O_6$.**—Dissolve 10 gms. of glycerol and 35 gms. of crystalline soda in 60 c.cs. of warm water. Cool to room temperature and add slowly 15 gms. (5 c.cs.) of bromine. Shake well after each addition. Carbon dioxide is evolved, and in half an hour the reaction will be over.

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To test for the glycerose treat with sulphuric acid till the colour of bromine appears, render alkaline again and add Fehling's solution.

The osazone may be prepared in the usual way.

Note.—The above reaction gives rise to a mixture of sugars, in which *i*-fructose predominates. This was named α-acrose by E. Fischer, who was the first to carry out the reaction.

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CHAPTER XIII.

THE CARBOHYDRATES.

1. **Reduction of a hexose to a hexite.**

$$\text{Arabinose to arabinite; } \left.\begin{matrix}\text{mannose}\\ \text{glucose}\end{matrix}\right\}\text{to mannite.}$$

$$CH_2OH.(CHOH)_4.CHO \longrightarrow CH_2OH.(CHOH)_4.CH_2OH.$$

Dissolve 15 gms. of the sugar in 200 c.cs. of water and add 300 gms. of 3 % sodium amalgam in small portions, keeping the liquid just acid with dilute sulphuric. When sufficient amalgam has been used (many hours are necessary) Fehling's solution will no longer be reduced. Separate the mercury, boil the *neutral* solution till crystallisation begins. Then mix whilst hot with an equal volume of 90 % alcohol, filter hot and set aside. The hexite crystallises out.

2. **Oxidation of a sugar to an acid.**—Glucose to gluconic acid; arabinose to arabonic acid.

$$CH_2OH.(CHOH)_4.CHO \longrightarrow CH_2.OH.(CHOH)_4.COOH.$$

Mix a concentrated solution of 1 part of sugar with 2 parts of nitric acid, S.G. 1·2, and maintain at 35° for 6 hours. The solution is then diluted and warmed with calcium carbonate till neutral. Filter and crystallise the calcium salt, treat with the requisite quantity of sulphuric acid, and extract the filtered liquid with ether.

3. **Kiliani's synthesis of a hexose from a pentose, a heptose from a hexose etc.**

Scheme.—Hexose ⟶ cyanhydrin ⟶ heptolactone ⟶ heptose.

Preparation of glucoheptose from glucose.

(*a*) **Preparation of the heptolactone.**—100 gms. of glucose are dissolved in 500 c.cs. of 3 % aqueous hydrocyanic acid, and 1 c.c. of strong ammonia added. The mixture is kept at 25° for several days, when the liquid turns brown and the smell of prussic acid almost disappears. The liquid is now boiled quickly and then treated with 134 gms. of crystallised baryta in 400 c.cs. of water. Warm until the smell of ammonia disappears, acidify the hot liquid with sulphuric acid, boil off unchanged hydrocyanic acid, ppt. the remainder of the barium as sulphate and evaporate the filtrate in an open dish to a thick syrup (excess of sulphuric acid must be avoided). Leave for several days

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till the heptolactone has crystallised, and wash away the dark mother-liquor with 80 % alcohol. Filter at the pump. Yield, about 30 gms.

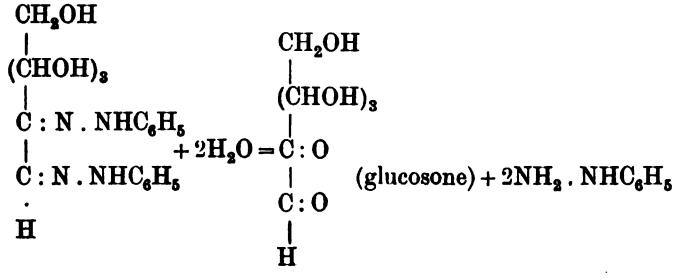
(*b*) **Reduction of the lactone to the heptose.**—Dissolve 30 gms. of the lactone in 300 c.cs. of water in a 1½ litre flask. Cool in ice and salt, add 4 c.cs. of dilute sulphuric acid and then 200 gms. of 2½ % sodium amalgam. Continue to add sulphuric acid at such a rate that the liquid is just acid, and cool in the freezing mixture during the whole reaction. When the amalgam has been used up add a further 200 gms., and proceed as before till 600 gms. in all have been added. This will have required about an hour. Separate from the mercury and render alkaline with enough caustic soda to cause an alkaline reaction after standing for half an hour. Any unchanged lactone is thereby converted to the sodium salt of the acid. Neutralise with sulphuric acid, decolorise by shaking and warming with animal charcoal and filter. Add to the filtrate 8 times its volume of absolute alcohol, shake and set aside for 12 hours. The sodium salts of the organic acids are thereby pptd. Filter and distil off the alcohol from a water-bath. The remaining aqueous solution is evaporated (finally on a water-bath) to crystallisation. Filter on the pump, wash with 50 % alcohol and finally with absolute alcohol.

4. **Transformation of an aldose to a ketose.**

Scheme.—Aldose ⟶ osazone ⟶ osone ⟶ ketose.

Glucose to fructose. (*a*) For preparation of glucosazone see Chapter IV.

(*b*) *Hydrolysis of glucosazone to glucosone.*—To 10 gms. of finely-powdered glucosazone add 100 c.cs. of fuming hydrochloric acid. The mass turns dark red and the same colour is imparted to the solution. Add an equal volume of water, warm to 40° and shake violently. A clear solution is obtained from which phenyl-hydrazine hydrochloride will crystallise on cooling. Set aside for 10 minutes, filter, cool to 0° and remove the hydrochloric acid by adding lead carbonate. Filter. Use the solution without further purification.



(*c*) *Glucosone to fructose.*—To the above solution add an equal volume of water and 100 gms. of zinc dust. Shake till well mixed, add 30 gms. of glacial acetic acid and heat to 100° for an hour. Ppt. the zinc with hydrogen sulphide and evaporate the filtrate *in vacuo*. The residue is taken up with alcohol and filtered. By addition of ether the fructose is obtained as a syrup.

5. **The reverse process, ketose ⟶ aldose.**

Scheme.—Ketose ⟶ hexite $\xrightarrow{\text{(oxidation)}}$ lactone $\xrightarrow{\text{(reduction)}}$ aldose.

Perform each step by the methods already described above.

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Properties of the more common carbohydrates.

Arabinose, $C_5H_{10}O_5$.—1. Rhombic prisms. M.P. of arabinose, 159°. Soluble in water. Solution strongly dextrorotatory. Soluble in 90 % alcohol, but not very soluble in absolute alcohol. Osazone melts at 159°.

Pentoses generally.

2. Reduce Fehling's solution and ammoniacal silver oxide. Turn brown on warming with alkali.

3. When the solution is distilled with an equal volume of strong hydrochloric acid, furfuraldehyd is formed. This gives a red colour with aniline acetate.

Note.—Glucose, maltose, and, to a small extent fructose, also give this test.

4. To a few c.cs. of a saturated solution of phloroglucinol in hydrochloric acid of S.G. 1·2 add a few drops of the pentose solution. A bright cherry-red colour is produced. (Distinction from glucose and maltose.)

Glucose ($C_6H_{12}O_6$).—1. Crystallises with 1 molecule of water (M.P. 86°), or anhydrous from alcohol (M.P. 146°). Usually met with as brownish lumps. Fairly sweet. Solution dextrorotatory.

2. On heating alone it chars. Heated with sulphuric acid it chars slowly. Warmed with alkali solution it gives a yellow colour changing to brown on boiling. (Cf. Sucrose).

3. It reduces Fehling's solution and gives the silver mirror test. It also reduces Barfoed's reagent. (Cf. Maltose.)

4. It gives an osazone of M.P. 204°.

Galactose ($C_6H_{12}O_6$).—1. Hexagonal plates, M.P. 165°. Less soluble than glucose.

2. Reduces Fehling's solution and ammoniacal silver oxide.

3. Its osazone melts at 193°-194°.

Fructose (*Laevulose*), ($C_6H_{12}O_6$).—1. Crystalline masses, needles. M.P. 95°. Soluble in water, alcohol and a mixture of alcohol and ether. (Distinction from glucose.)

2. Readily reduces Fehling's solution.

3. Its osazone is identical with glucosazone.

4. With a strong solution of hydrobromic acid in dry ether it gives gradually a deep purple colour, due to bromo-methyl-furfural,

$$C_4H_2O(CH_2Br)CHO.$$

(Distinction from glucose.) This reaction is characteristic of ketoses.

Maltose ($C_{12}H_{22}O_{11}$).—1. White crystalline solid. Soluble in water, insoluble in absolute alcohol. Readily chars when heated alone or with sulphuric acid.

2. With alkalis it behaves like glucose.

3. With Fehling's solution, etc., it behaves like glucose.

4. It does not reduce a solution of copper acetate with a little acetic acid (Barfoed's reagent). Difference from glucose.

5. Its osazone melts at 190°-191°, and does not crystallise till reaction mixture is cooled.

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Lactose (milk sugar), $C_{12}H_{22}O_{11} . H_2O$.—1. Hard, white prisms. Not very sweet, and feel "gritty" in the mouth. Soluble in water, not in alcohol or ether. M.P. 203°-204°.

2. Chars when heated alone or with sulphuric acid.

3. With alkalis, Fehling's solution and Barfoed's reagent it behaves similarly to maltose.

4. Its osazone, formed only after cooling and standing aside the reaction mixture, melts at 200°.

Sucrose (cane sugar), $C_{12}H_{22}O_{11}$.—1. Monoclinic crystals. Very sweet. Soluble in water, not in alcohol or ether. M.P. 160°.

2. Chars readily when heated alone or with sulphuric acid, with evolution of carbon and sulphur dioxides.

3. No action with alkalis, Fehling's or Barfoed's reagents.

4. After "inversion," brought about by heating for some time with dilute acid, it gives all the tests mentioned in 3.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6)} + \underset{\text{(fructose)}}{C_6H_{12}O_6}.$$

5. No osazone is obtained unless the action is much prolonged, when inversion will take place.

Starch $(C_6H_{10}O_5)x$.—1. White tasteless powder. Insoluble in cold water, forms an opalescent solution with boiling water. Filtered and pptd. with alcohol the so-called "soluble starch" is obtained. Examined under the microscope the grains have characteristic appearances according to their source. Examine and remember the appearance of rice, potato, wheat and rye starch.

2. Heated to above 110° it gives dextrin, soluble in water (see below).

3. Treated with a drop of iodine solution in potassium iodide an intense blue colour is obtained. This disappears on heating and reappears on cooling the solution.

4. Boiled with dilute sulphuric or hydrochloric acid it gives glucose, which may be tested for.

Dextrin (British gum), $C_6H_{10}O_5$.—1. White powder, forming a gummy solution with water.

2. Dextrin occurs in several varieties, of which the two chief ones are amylo-dextrin or soluble starch, giving a blue colour, and erythro-dextrin, giving a red colour, with iodine solution in potassium iodide. The latter reduces Fehling's solution.

Cellulose $(C_6H_{10}O_5)x$.—1. Chief constituent of cell-walls of all plants. It occurs in a variety of forms. Those best known are pure filter-paper and cotton-wool.

2. It is soluble in ammoniacal copper hydroxide solution and in other reagents. Acids ppt. it from the first-named solvent.

3. It gives no blue colour with iodine alone, but it does with Schultze's reagent (concentrated zinc chloride containing some potassium iodide and iodine).

4. Grind in a mortar with a few drops of strong sulphuric acid. Dilute largely and boil. Various substances are obtained, amongst which glucose may readily be recognised by Fehling's test, etc.

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CHAPTER XIV.

SYNTHESES FROM ACETO-ACETIC AND MALONIC ESTERS.

1. **Preparation of aceto-acetic ester** (Conrad, *A.* **186**, 214).—Dry some ethyl acetate (250 gms.) by (*a*) shaking with a saturated solution of calcium chloride (removes any alcohol and acetic acid); (*b*) standing overnight with fused calcium chloride and distilling after filtering. To 200 gms. of the dry ester add 20 gms. of sodium in small pieces, a few at a time, with cooling. Boil gently on a water-bath (reflux) for 2½ hours, till the sodium has entirely dissolved. Whilst still warm add 110 gms. of 50 % acetic acid and shake. Then add 200 c.cs. of saturated brine and shake again. Separate the upper layer, wash it with a little water and distil with a free flame and wire gauze. At 95° discontinue and subject the residue to distillation under reduced pressure. At a pressure of 18 mm. the B.P. is 79° (Gattermann).

(From the distillate below 95° at ordinary pressure the unchanged ethyl acetate may be recovered in the usual way.)

Properties.—1. Liquid. B.P. 181°. S.G. 1·025 at 20°.

2. It reacts with sodium, giving derivatives in which the sodium will react with halogen in almost any organic compound. The products can be hydrolysed at will to ketones or acids, as described below. For other reactions consult a theoretical text-book. Below are outlined the ketone and acid syntheses.

Preparation of the sodium derivative of aceto-acetic ester.—10 gms. of sodium are dissolved in 100 gms. of absolute alcohol. An equal volume of anhydrous ether (dried and distilled from sodium) is now added, and then a mixture of 56·5 gms. of aceto-acetic ester and 56·5 gms. of anhydrous ether. It is not usual to isolate the sodium compound, but the mixture is used in the required synthesis without further treatment. The calculated quantity of alkyl or other halide is added, the ppt. of sodium chloride, etc., filtered off, and the resulting ester may be:

(1) Treated with another atom of sodium followed by another molecule of halide.

(2) Hydrolysed by cold dilute alkali, when the free acid (sodium salt) is obtained, which on heating gives a ketone.

(3) Hydrolysed by hot concentrated alcoholic alkali, when a substituted acetic acid is obtained.

The scheme is outlined below.

$$CH_3 . CO . CH_2 . COOEt + NaOEt = CH_3 . CO . CHNa . COOEt + EtOH.$$

$$CH_3 . CO . CHNa . COOEt + 1C_2H_5 = NaI + CH_3 . CO . \underset{\underset{Et}{|}}{CH} . COOEt$$

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The other hydrogen atom may then be similarly replaced.

Hydrolysis (2) above may be formulated thus :

$$\underset{\dot{E}t}{CH_3 . CO . CH . COOEt} + H_2O = \underset{\dot{E}t}{CH_3 . CO . CH . COOH} + EtOH.$$

This acid on heating evolves CO_2 thus, and leaves the desired ketone :

$$\underset{\dot{E}t}{CH_3 . CO . CH . COOH} \longrightarrow CO_2 + CH_3 . CO . CH_2 . C_2H_5.$$

Thus any ketone of which one of the groups attached to $-CO-$ is methyl may be prepared.

Hydrolysis (3) above is as follows :

$$\begin{array}{l} CH_3 . CO . CH . COOEt \\ \qquad\qquad \dot{E}t. \\ \quad HOH \qquad\quad HOH \end{array} = CH_3COOH + Et . CH_2 . COOH + EtOH.$$

Thus any fatty monocarboxylic acid may be prepared.

By condensing with a chlorine-substituted ester any dibasic acid may be prepared, *e.g.*

$$\begin{array}{l} \quad HOH \qquad\qquad HOH \\ CH_3 . CO CH . CO . O Et \\ \qquad\quad \dot{C}H_2 \\ \qquad\quad \cdot\ HOH \\ \qquad\quad COOEt \end{array}$$

hydrolyses as indicated.

2. **Syntheses with malonic ester.**—The reactions are very similar to those with aceto-acetic ester.

(*a*) *Preparation of malonic ester* (Venables, Claisen, *A.* **218**, 131). See Chapter XI., p. 338.

(*b*) *Preparation of the substituted ester, via the sodium compound. Ethyl malonic ester.*—Into 50 gms. of absolute alcohol in a small flask fitted with a reflux drop gradually 4-6 gms. of sodium in small pieces. Cool, add little by little 32 gms. of malonic ester, shake well and then add 40 gms. of ethyl iodide. Heat on the water-bath till the alkaline reaction disappears (1-2 hours). Distil off the alcohol on a water-bath, just dissolve the residue in water, extract with ether and fractionate the ethereal solution. Ethyl malonic ester boils at 207°.

(*c*) *Hydrolysis of the ester.*—To 15 gms. of ethyl malonic ester, in a flask with a reflux, add gradually through the reflux a cooled solution of 20 gms. of potash in 30 gms. of water. The whole sets to a solid mass, which is heated on a water-bath. A violent reaction ensues. Continue the heating till all oily drops disappear.

(*d*) *Preparation of ethyl malonic acid.*—Cool the above solution, dilute it with 50 c.cs. of water and add just enough strong hydrochloric acid to make the solution acid. Extract twice with ether, dry with anhydrous sodium sulphate, distil off the ether on the water-bath. Carefully warm the residue on the water-bath till it solidifies. Cool and dry with filter-paper.

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(*e*) *Preparation of butyric acid.*—Place the ethyl malonic acid in a distilling flask and attach the side tube to an air condenser. Arrange so that the condenser slopes upwards and acts as a reflux. Fit the flask with a cork and a thermometer and heat on an oil-bath or fusible metal bath to 180°. When the evolution of carbon dioxide has ceased, distil in the usual way and collect the portion 160°-164°.

$$\begin{array}{l} COOEt \\ CH_2 \\ \dot{C}OOEt \end{array} \longrightarrow \begin{array}{l} COOEt \\ \dot{C}HNa \\ \dot{C}OOEt \end{array} \longrightarrow \begin{array}{l} COOEt \\ \dot{C}H\,.\,Et \\ \dot{C}OOEt \end{array} \longrightarrow \begin{array}{l} COOH \\ \dot{C}H\,.\,Et \\ \dot{C}OOH. \end{array}$$

and then

$$\begin{array}{l} COOH \\ \dot{C}H\,.\,Et \\ \dot{C}OOH. \end{array} \longrightarrow CO_2 + EtCH_2\,.\,COOH.$$

Thus any substituted malonic acid or any acid of the monocarboxyl fatty series may be synthesised. Malonic acid itself when heated gives acetic acid.

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CHAPTER XV.

SYNTHESES BY THE USE OF GRIGNARD'S REAGENT.

ALL alkyl halides react with magnesium in dry ether and form compounds of the type R . Mg . I (Grignard, *C.R.* **130**, 1322 (1900); **132**, 336 (1901).

Preparation of the reagent. (*The ether must have been dried over and distilled from sodium.*)—Mix 36 gms. of methyl iodide and 50 c.cs. of absolute ether. Add 20 c.cs. of this mixture to 6 gms. of clean magnesium ribbon or filings in a dry 250 c.c. flask fitted with a reflux. If the reaction does not commence add a trace of iodine. When it is complete add 50 c.cs. of dry ether, then the rest of the iodide ether mixture very slowly. Boil the whole for half an hour (water-bath), and if the magnesium has not all dissolved add a few drops of methyl iodide.

If an aromatic halide is used the reaction is much slower.

According to Baeyer and Villiger, a compound of the type

$$R . Mg . I + (C_2H_5)_2O$$

is formed.

Tschelinzett (*B.* **37**, 4539 (1904) recommends the use of absolute benzol instead of ether. The mixture is heated on the water-bath as above. When the reaction starts allow it to proceed to the end. (Iodine assists the reaction.) Afterwards a little ether is added. A guard tube of calcium chloride on the top of the reflux prevents access of moisture.

The following reactions may be carried out with the reagent:

Treated with an	aldehyd	and the product hydrolysed				⟶ 2ry alcohol.
,,	,,	ketone	,,	,,	,,	3ry alcohol.
,,	,,	ester / acid chloride	,,	,,	,,	3ry alcohol.
,,	,,	halide	,,	,,	,,	hydrocarbon.

In addition we shall describe

Synthesis of carboxylic acids.

Additive compounds with unsaturated ketones. (Kohler, *Am. Ch. J.*, 1905 (**33**), 153, 333; (**34**) 132.

Reformatsky's reaction.

This by no means exhausts the list of reactions of this most versatile reagent. For complete references see *Ann. Rep.* each year under "Grignard's reaction."

1. **Preparation of a 2ry alcohol from an aldehyd.** *Phenyl methyl carbinol*, $C_6H_5)(CH_3)CH . OH$.—The reagent prepared as described is cooled with ice

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and a solution of 26 gms. of benzaldehyd in its own volume of absolute ether is added slowly through the reflux with constant shaking. Stand overnight (calcium chloride tube on condenser!) and next morning add dilute hydrochloric acid with constant cooling in water till the whole of the solid matter has gone into solution. Remove the ethereal layer, extract again with ether and mix the two extracts, which are washed in succession with (1) sodium bicarbonate solution; (2) sodium bisulphite solution; (3) sodium bicarbonate again. It is then dehydrated by standing with anhydrous sodium sulphate, the ether distilled off and the carbinol distilled under reduced pressure. The boiling point at 15 mm. is 100°, and the yield 70 % of theory.

The reactions may be formulated thus:

$$C_6H_5.C\begin{cases}H\\O\end{cases} + CH_3MgI \longrightarrow C_6H_5.C\begin{cases}H\\OMgI\\CH_3\end{cases}, \text{ which } + HCl$$

$$\longrightarrow C_6H_5.C\begin{cases}H\\OH\\CH_3\end{cases} + MgICl.$$

In an exactly similar manner **benzhydrol**. $C_6H_5C\begin{cases}H\\OH\\C_6H_5\end{cases}$ may be made from 3 gms. of magnesium, 19·6 gms. of brom-benzene, 50 c.cs. of ether and 13 gms. of benzaldehyd in 30 c.cs. of ether. It is a crystalline mass, M.P. 68°. Yield, 70 % of theory.

Using chloral and methyl iodide, tri-chlor-2^{17} propyl alcohol is obtained. M.P. 49·2°; B.P. 150°-160°.

2. **Preparation of a 3^{17} alcohol from a ketone.** 3^{17} *butyl alcohol from acetone.*—Prepare just as in 1, from 4·8 gms. of magnesium, 29 gms. of methyl iodide, 50 c.cs. of absolute ether, and with ice-cooling drop in 12 gms. of acetone in 20 gms. of ether. Every drop causes a ppt. which quickly dissolves; finally a green-grey mass collects at the bottom of the flask. Leave overnight, then shake with small pieces of ice and add 33 % acetic acid till the ppt. is all dissolved. Separate the two layers, distil off the ether and add the alcohol to the mother-liquor again. Now distil in steam until the distillate no longer becomes cloudy on adding potassium carbonate. Then salt out with potassium carbonate, remove the oily layer, dry with fused potassium carbonate and redistil from a water-bath. Allow the distillate to stand 48 hours with barium oxide, and distil from this. B.P. 79°-82°.

3. **Preparation of 3^{17} alcohol from an ester or acid chloride** (Grignard, *C.R.* **132**, 336 (1901)). *Di-phenyl-tolyl-carbinol from m-toluic methyl ester.*—39·3 gms. of *m*-toluic acid methyl ester are added to 12·6 gms. of magnesium, 88·2 gms. of brom-benzene and a trace of iodine in ether solution as before. The ester is added dropwise in the cold. Warm to complete the reaction, add dilute sulphuric as before, remove the ethereal layer and distil off the ether; the unchanged brom-benzene and ester are removed by distilling in steam till no more oily drops come over, and the residue recrystallised from benzene. Yield, 80 % of theory.

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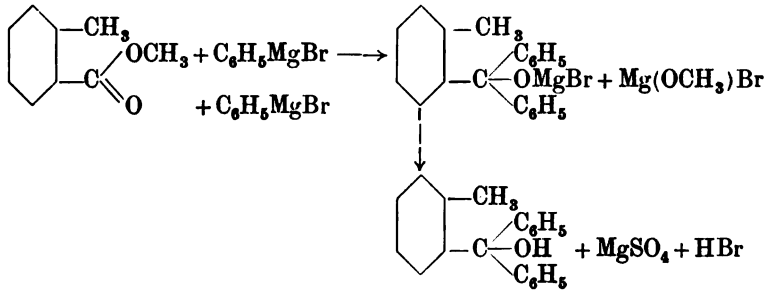
Scheme:



4. **Preparation of a hydrocarbon** (Benzene series).—The magnesium, ether and aryl bromide are mixed as before. When the magnesium has dissolved add the theoretical quantity of methyl (ethyl) sulphate or iodide in dry ether. When the action is over, pour on to ice, distil off the ether and steam-distil the residue. Yield, 70 % of theory. (Werner and Zilkins, *B.* 1903, **36**, 2116.)

$$C_6H_5MgBr + IC_2H_5 = \underset{\text{(ethyl-benzene)}}{C_6H_5 . C_2H_5} + MgBrI.$$

5. **Synthesis of a carboxylic acid** (Grignard, *B.* **35**, 2519). *Benzoic acid from iodo-benzene.*—2·4 gms. of magnesium ribbon, 20·4 gms. of iodo-benzene, 40 gms. of absolute ether are mixed as before. Cool and saturate with a rapid stream of carbon dioxide for 3 hours. The carbon dioxide must be dried by at least two Woulff's bottles of strong sulphuric acid, or, better, by a tower filled with glass beads moistened with the acid.

Then add some ice and a mixture of 15 c.cs. of strong hydrochloric acid and 15 c.cs. of water. Extract with ether (3 times), shake the ether extract with alkali and ppt. the benzoic acid from this by acidifying with hydrochloric acid. Yield, 10-11 gms.

$$C_6H_5MgI + CO_2 \longrightarrow C_6H_5 . C\begin{matrix}\diagup O \\ \diagdown OMgI\end{matrix} \longrightarrow$$

$$C_6H_5C\begin{matrix}\diagup O \\ \diagdown OH\end{matrix} + MgICl.$$

6. **Reformatsky's reaction** (Perkin, *J.C.S.*, 1896, 69, 1482).—*Synthesis o an oxyacid.*

$$(CH_3)_2CO + CH_3 . CHBr . CO . OC_2H_5 + Mg.$$

$$\longrightarrow (CH_3)_2C\begin{matrix}\diagup OMgBr \\ \diagdown CH(CH_3) . COOC_2H_5\end{matrix} \longrightarrow (CH_3)_2 . C\begin{matrix}\diagup OH \\ \diagdown CH . COOC_2H_5 \\ \quad\;\; \dot{C}H_3\end{matrix}.$$

90 gms. of acetone, 182 gms. of ethyl-α-bromo-propionate are mixed in a flask fitted with a reflux, and magnesium ribbon added. Warm on a water-bath. A brisk action ensues. Cool. Add more magnesium as the reaction subsides, and continue as before till some magnesium remains undissolved. Heat on a water-bath for 3 hours and treat the product with water and dilute sulphuric acid as before. Extract the ester with ether, distil off the ether and distil under reduced pressure.

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PART III.

PREPARATIONS IN THE AROMATIC SERIES.

CHAPTER I.

ACTION OF HALOGENS.

UNDER different conditions chlorine acts on benzene in three ways.

(1) Addition - 3 molecules, add to 1 molecule of benzene.

(2) Substitution { (*a*) Boiling, in sunlight, in the *side-chain*.
(*b*) In the dark with a catalyst (halogen-carrier) in the *nucleus*.

1. **Preparation of the addition products, $C_6H_6 . Cl_6$** (α and β forms), α or *trans*-derivative (Matthews, *Soc.*, **59**, 166.)—Pass chlorine into a mixture of benzene and 1 % caustic soda to saturation. Leave overnight. Filter on the pump. Add warm water to the crystals and distil them in steam.

The α-derivative only goes over and crystallises in the receiver.

Properties.—1. Monoclinic crystals. M.P. 157°; B.P. 288°.

2. On keeping they are transformed to hydrochloric acid and 1-2-4- trichlor-benzene.

β or *cis*-derivative is obtained by passing chlorine into a solution of benzene in chloroform. It melts and sublimes at 310°.

Substitution of halogen in the nucleus.

2. **Preparation of chloro-benzene** (Beilstein, *B.* 1896, ii. 43).—Fit up an apparatus as for the chlorination of acetic acid, Fig. 98, p. 332. Put 50 gms. of benzene in the retort and add a little molybdenum pentachloride, iodine, or aluminium-mercury couple (made by treating aluminium foil clippings with mercuric chloride solution and washing with water, alcohol and drying). Weigh the retort and its contents.

Dry chlorine is passed into the *cold* benzene through a tube fitted to the tubulus of the retort, until there is an increase in weight of 22 gms. Then stop, shake the product in a separating funnel with dilute caustic soda till free from hydrochloric acid and distil. Collect the fraction 130°-135°.

Properties.—1. Colourless liquid. B.P. 132°; S.G. 1·12 at 0°.

2. The chlorine is inert and does not react with reagents as does chlorine in an alkyl group.

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Note.—By similarly chlorinating toluene, *o*- and *p*-chlor-toluene can be obtained. (Hübner, *B.* **6**, 790; Seelig, *A.* **237**, 152.) Separate by fractionation. B.P's. *ortho*-derivative, 156°; *para*-, 163°.

3. **Preparation of bromo-benzene.**—A flask is fitted with a tap-funnel and a reflux condenser to which is attached a tube terminating with a funnel in a vessel of alkali as in the previous preparation, to absorb the hydrobromic acid evolved. The benzene is placed in the flask and some iron filings added as a carrier. Add the correct amount of bromine gradually from the tap-funnel; then warm on a water-bath, shake with caustic soda solution and distil in steam. Collect as long as oily drops which *sink* come over (those which *float* are unchanged benzene). Separate, dry with calcium chloride and rectify. B.P. 150°-160°.

Substitution by halogen in the side-chain.

4. **Preparation of Benzyl chloride, $C_6H_5 . CH_2Cl$** (Cannizzaro, *A. Ch.* (3), **45**, 768; Beilstein, *A.* 139, 337).—Set up an apparatus similar to that for preparing chlorobenzene, but with a wire gauze under the retort. Pass dry chlorine into 50 gms. of *boiling* toluene to which 2 gms. of phosphorus pentachloride have been added, until the mixture has increased in weight by 19 gms. Then fractionate, collecting separately the portion 165°-188°. Refractionate this, collecting the portion 176°-180°. Yield, about 80 % of the toluene used. The phosphorus pentachloride hastens the reaction, which should be carried out in sunlight if possible.

Properties.—Pungent-smelling liquid. B.P. 177°-178°; S.G. ·945. *Avoid getting it on the hands.* This applies to all these halogen derivatives. A painful burning sensation is felt for some time after contact with them.

5. **Preparation of benzal chloride, $C_6H_5CHCl_2$** (Colson Gautier, *A. Ch.* (6), **11**, 21).—Continue the previous preparation to a 76 % increase in the weight of toluene taken. Proceed as before, collecting the fraction at 190°-220° and refractionating at 210°-214°.

Properties.—Liquid. B.P. 212°-214°; S.G. 1·295 at 16°. Can be hydrolysed to benzaldehyd.

6. **Preparation of Benzo-trichloride, $C_6H_5 . CCl_3$** (Limpricht, *A.* **135**, 50; **139**, 323).—As before, to an increase of 114 % of the weight of toluene. Fractionate and collect the portion 212°-215°.

Properties.—Liquid. B.P. 213°-214°. Easily hydrolysed to benzoic acid.

Iodo-benzene must be made indirectly (p. 369).

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CHAPTER II.

SYNTHESES OF BENZENE HOMOLOGUES.

1. **Fittig's synthesis of a hydrocarbon.**

Ethyl Benzene (Tollius, Fittig, *A.* **131**, 310).
2^{ry} Propyl Benzene (Jacobsen, *B.* **8**, 1260).

This is similar to the Wurtz reaction for the synthesis of paraffin homologues.

In a flask connected with a reflux condenser, and standing in an ice-bath, place 80 c.cs. of sodium-dried ether and add 40 gms. of bromobenzene and 36 gms. of ethyl bromide or 40 gms. of 2^{ry} propyl bromide. Then through the reflux add 20 gms. of sodium in thin slices, a little at a time. Then warm for 10 minutes till the sodium has ceased to react, stand overnight and decant the liquid from the blue mass that is left. *Throw this residue away out of doors.* Distil the ethereal solution on the water-bath, and when the ether has evaporated, fractionate the residue and collect. B.P. ethyl benzene at 134°; 2^{ry} propyl benzene at 152°-153°.

2. **Friedel and Craft's method.**

$$C_6H_6 + C_2H_5Br = HBr + C_6H_5 . C_2H_5$$

under the influence of anhydrous aluminium chloride.

Connect a dry distilling flask to a condenser. Arrange so that the condenser slopes upwards and from the end of it lead a tube which dips into a flask containing water, which is weighed and guarded with a horizontal calcium chloride tube.

Four or five times the theoretical amount of the benzene hydrocarbon is introduced, followed by the alkyl halide (theoretical quantity desired). Introduce now about 15 gms. of finely-powdered anhydrous aluminium chloride. Cork the flask. If the reaction does not start, warm gently till it does. When it slackens, add more aluminium chloride until the amount of hydrogen halide evolved and collected in the weighed flask of water is that demanded by theory. Then cool and pour the mixture into excess of dilute hydrochloric acid, separate the supernatant hydrocarbon, wash with water and dry over calcium chloride. Rectify.

The yield is about 90 % of the desired hydrocarbon, but di-substitution products are also produced.

Try 7 parts of ethyl bromide, 12 of benzene and 1 of aluminium chloride.

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CHAPTER III.

SULPHONATION.

1. Preparation of benzene sulphonic acid and its salts.

Mitscherlich, *Pogg Ann.* **31**, 283, 631.
Gattermann, *B.* (1891) [24], 2121.

There are several methods of sulphonation. The aim of the refinements is to shorten the time required.

(*a*) *By concentrated sulphuric acid.*—Heat on a sand-bath in a 500 c.c. flask connected with a reflux, a mixture of equal volumes of benzene and of pure sulphuric acid, S.G. 1·84, till the benzene has gone into solution. At least a day will be required.

(*b*) *By fuming sulphuric acid.*—In a flask connected with a reflux, place 100-150 gms. of fuming sulphuric acid of S.G. 1·88-9, corresponding to 5-8 % excess of anhydride. Add gradually through the reflux, with constant shaking, 30-40 gms. of benzene. Cool well, and let each portion dissolve before adding the next. About 15 minutes will be required. If the benzene refuses to dissolve, warm to 40°-50°.

(*c*) *By the aid of porous material* (*intimate mixture*).—50 gms. of benzene and 250 gms. of pure sulphuric acid are made into a stiff paste with kieselgühr. Leave for 24 hours and then mix with two litres of water by adding the paste in small quantities to the water.

Whichever of the above methods is used, the solution is next treated either for the sodium, calcium or barium salt.

(i) To obtain the sodium salt, add the solution slowly through a separating funnel to four times its volume of a saturated salt solution contained in a large ice-cooled beaker. The sodium benzene sulphonate separates gradually in leaflets and the crystallisation is hastened by rubbing the sides of the beaker with a glass-rod. Filter at the pump, wash with brine, press between filter-paper and dry at 110°. Recrystallise from absolute alcohol.

Note. A by-product, sulphobenzite, $(C_6H_5)_2SO_3$, is also formed. This may be extracted from the crude salt with warm ether. Crystals. M.P. 129°.

(ii) To obtain the alkali-earth salt, pour the reaction mixture into 600 c.cs. of water and neutralise it whilst hot with a paste of the required carbonate and water. Filter hot, evaporate halfway and cool.

(iii) If the free acid is required, add to a hot solution of a weighed quantity of the barium salt the calculated quantity of dilute sulphuric acid. Filter. Evaporate to a small bulk and allow to crystallise.

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Properties.—1. White deliquescent solid. M.P. 100° C.

2. Strong acid. Heated with soda-lime it gives the characteristic smell of phenol, which is manufactured in this way from benzene.

Note.—Homologues of benzene, and substitution products, are sulphonated far more easily than benzene itself. (See naphthalene and phenol sulphonic acids.)

2. **Derivatives of benzene sulphonic acid.** (i) *Benzene sulphon-chloride* (Otto, *Z.* **1866**, 106).

$$C_6H_5 . SO_3Na + PCl_5 = C_6H_5 . SO_2Cl + NaCl + POCl_3.$$

Shake together in a dry flask in the fume-cupboard the above quantities of the reagents, adding the sodium salt gradually to the chloride. Warm for 20 minutes on a water-bath. Cool and pour into water. The chloride separates as an oil (not readily acted on by water). Separate and distil under reduced pressure. B.P. 120° under 10 mm., 246°-247° at ordinary pressure.

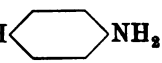
(ii) *Benzene sulphonamide* (Gerhardt, Chancel, *J.* **1852**, 434).—Rub together in a mortar 1 c.c. of benzene sulphonchloride with 10-12 gms. of powdered ammonium carbonate. Heat gently in a basin with constant stirring till the odour of the chloride has gone. Cool, add water, filter on the pump, wash the residue with water and crystallise from alcohol by dissolving and then adding warm water till turbidity appears, finally allowing to cool M.P. of crystals, 156°.

3. **Preparation of the phenol sulphonic acids** (Kekulé, *Z.* 1867, 199).—According to Crum Brown and Gibson's rule, the ortho and para acids will be formed.

Take equal quantities of phenol and concentrated sulphuric acid, melt the phenol on a water-bath and add it to the acid in a large basin. After about an hour dilute with water and neutralise with white lead. Filter from the lead sulphate and obtain the potassium salts by adding potassium carbonate.

On evaporating to crystallisation the *p*-salt crystallises first in water-free leaflets; then the *o*-salt in efflorescent crystals $+\frac{3}{4}H_2O$. Separation may be effected to some extent by spreading out and picking out the crystals which effloresce.

If the reaction be performed at 110° the product is practically all the *p*-acid.

4. **Sulphonation of an amine.** *Sulphanilic acid,* 

(Gerhardt, *A.* (1846) **60**, 312).—To 64 gms. of pure sulphuric acid in a 200 c.c. round-bottomed flask add gradually 20 gms. of aniline with constant shaking. Heat for 4-5 hours on an oil-bath at 180° till no aniline separates from a test portion when diluted and made alkaline with caustic soda. Cool and pour into cold water. The acid separates as a crystalline mass. Filter, wash with cold water and recrystallise from hot water, decolorising with animal charcoal if necessary. Yield, 20-25 gms.

Properties.—1. Colourless crystals $+ H_2O$, efflorescent. M.P. indefinite.

2. Diazotised (*q.v.*) and added to a drop of dimethyl-aniline, a thick yellowish brown ppt. of methyl orange is obtained.

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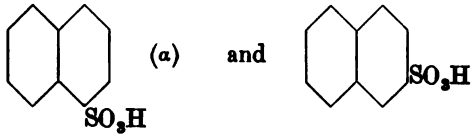
5. Preparation of the naphthalene sulphonic acids.



(α) and (β)

At lower temperatures mainly the α acid is formed, at higher ones the β. The salts of the β acid are less soluble than those of the α, and may be separated by fractional crystallisation.

(i) *The α acid* (Merz, *B.* **3**, 196).—Heat 4 parts of naphthalene with 3 of pure sulphuric acid for 8-10 hours at 80°. Pour into 12 times its volume of warm water (care !). Filter from free naphthalene and neutralise with white lead or chalk whilst the liquid is boiling. Strain through a cloth before filtering. Evaporate to crystallisation. The first crop of crystals will be largely the β-salt (1 part of the calcium salt is soluble in 76 of water at 10°), the next crop will be mainly α (1 in 16·5 of water at 10°). It may be freed from β-salt by warming with 10-12 parts of alcohol, filtering from the insoluble β-salt and crystallising.

The free acid is obtained as for benzene sulphonic acid. M.P. 85°-90°. Or the lead salt may be dissolved and saturated with hydrogen sulphide.

(ii) *The β acid* (*ibid.*).—5 parts of naphthalene, 4 of sulphuric acid. Heat for 8 hours to 160°. Proceed as before.

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CHAPTER IV.

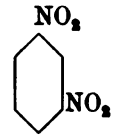
NITRATION.

NITRO-DERIVATIVES of benzene and its homologues, etc., form the basis of many modern high explosives. Like the action of sulphuric acid, benzene itself is more reluctant to react than its homologues and derivatives.

1. **Preparation of nitro-benzene, $C_6H_5NO_2$.**—Add slowly 100 gms. of nitric acid, S.G. 1·4, to 150 gms. (84 c.c.) of strong sulphuric acid in a 500 c.c. flask. Shake well, cool and add 50 gms. of benzene, a few c.cs. at a time, with constant shaking. Do not allow the temperature of the mixture to rise above 50°. When the benzene is all added (20-30 minutes) heat on a water-bath for half an hour with a vertical tube as reflux condenser. Cool, separate the *upper* layer of nitro-benzene and wash in the separating funnel with (1) water; (2) dilute sodium carbonate (the nitro-benzene is the *lower* layer when washing). Stand with *fused* calcium chloride till turbidity (water) disappears. Filter and distil, using an air condenser. Collect at 205°-208°. Yield, 60 gms.

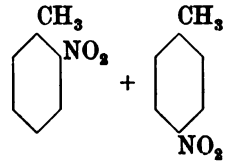
Properties.—Yellowish liquid, odour of bitter almonds. S.G. 1·21; B.P. 207°. Insoluble in water.

A little dinitrobenzene formed remains in the distilling flask.

2. **Preparation of *m*-dinitrobenzene.** 

—May be made from benzene by using more nitric acid and a higher temperature, but is more conveniently prepared from nitrobenzene.

Heat in a small flask fitted with a vertical tube as condenser, a mixture of 1 volume of strong sulphuric acid, 1 volume of nitrobenzene and 1½ volumes of strong nitric acid. After half an hour at 100° with frequent shaking, cool and pour into cold water. Filter the solid, press between filter-paper, dissolve in hot alcohol, add water till a turbidity appears, and set aside. Long yellow needles. M.P. 90°; B.P. 304°.

3. **Preparation of nitrotoluene.** 

(Beilstein, *A.* **155**, 1.)

—To 50 gms. of toluene in a flask add gradually a cooled mixture of 50 gms.

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of concentrated nitric acid and 75 gms. of sulphuric acid. The temperature should be kept between 20° and 30°. Wash the product with water then with dilute ammonia, and fractionate under reduced pressure with the aid of a fractionating column. When about 40 % has distilled, stop. The distillate is chiefly the *ortho*-body. The residue on cooling in ice and salt deposits the pure *para*-body. The distillate is again fractionated.

Properties.—Ortho. Liquid. B.P. 222°; S.G. 1.168. *Para.* Solid. M.P. 52°; B.P. 238°.

4. **Preparation of phenyl-nitro-methane, $C_6H_5 . CH_2NO_2$.**—Instead of the nucleus we may nitrate the side-chain by the method of Konowalow (*B.* **28**, 1865 (1895)).

Toluene is heated in a bomb-tube (like that for the Carius halogen determination, *q.v.*) for 5 hours at 105°-108° with six times its weight of dilute nitric acid of S.G. 1·075. The product is made alkaline with caustic potash, extracted with ether, and the alkali solution left, which contains the phenyl-nitromethane salt, is treated with carbon dioxide. A yellow oil settles out, which is extracted with ether. The yield is 50 % of theory. Distil in a vacuum after evaporating the ether. B.P. of pure product, 141° at ordinary pressure.

5. **Preparation of nitranilines.**—The *ortho*- and *para*-bodies may be made by nitrating aniline, first protecting the amine group by acylating it.

The *meta*-body is obtained by partial reduction of *m*-dinitrobenzene (see under Amines).

(i) *o-Nitraniline* (Lellmann, *A.* **221**, 6).—Heat 50 gms. of acetanilide with 150 gms. of fuming sulphuric acid for half an hour at 100°. Cool and add 100 gms. of 92 % sulphuric acid. Cool to 0° and add a mixture of 37 gms. of 63 % nitric acid and an equal volume of sulphuric acid. Cautiously add 140 c.cs. of water and heat for half an hour. The liquid is now fractionally pptd. by (1) 500 c.cs. of water, (2) filtering, (3) adding 500 c.cs. of water, (4) filtering, (5) adding 2 litres of water, (6) filtering.

The third ppt. is pure *o*-nitraniline; the first two may be extracted with ether.

Properties.—Orange-yellow needles. M.P. 71.5°.

Alternatively.—Dissolve 45 gms. of aniline in 22 gms. of glacial acetic acid. Dissolve 23 gms. of nitric acid, S.G. 1·5, and 1 gm. of urea in 23 gms. of hot glacial acetic acid. When cold add the acid mixture to the acetanilide solution and leave for 24 hours. Ppt. by 360 c.cs. of ice-cold water and add an ice-cold mixture of 1 volume of 50 % potash solution, 4 volumes of water, and 1 volume of alcohol. Filter and wash the ppt. with the above mixture, then with water; *p*-nitro-acetanilide remains on the filter, whilst the *ortho*-body goes into solution. After standing 24 hours the *ortho*-body will be hydrolysed and a ppt. of *o*-nitraniline falls.

(ii) *p-Nitraniline.*—Dissolve 50 gms. of acetanilide in 50 gms. of hot glacial acetic acid. Cool and mix with 200 gms. of strong sulphuric acid. Cool in a mixture of ice and salt and run in, with constant stirring, a mixture of 30 gms. of nitric acid, S.G. 1·48, and 60 gms. of strong sulphuric acid. On pouring the product on to crushed ice the *p*-body is pptd. Filter, wash and recrystallise from dilute alcohol. Yield almost theoretical. The product is now hydrolysed by dissolving in 2½ parts of strong hydrochloric acid, and

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render alkaline with caustic soda. Cool and set aside. Filter off the *p*-nitraniline, wash and recrystallise. M.P. 147°.

6. **Nitrophenols.** (i) *Preparation of o- and p-nitrophenol.*—50 gms. of melted phenol are added gradually to 70 c.cs. of nitric acid in 200 c.cs. of water in a large round-bottomed flask. Shake thoroughly all the time. On standing, a dark tarry oil separates. Stand overnight, separate the oil and wash with water. Distil in steam. The *o*-body is carried over, the *p*-body remains behind. If the condenser tube is likely to be stopped up by crystals condensing in it, allow the water to run out for a few moments. Filter the distillate when no more of the product distils; dissolve in warm alcohol, add water till turbid, and set aside to crystallise.

The residue is extracted repeatedly with boiling water, the extracts united, boiled with animal charcoal and filtered. Allow to crystallise. If unable to get rid of a little tarry matter, dissolve in caustic soda, concentrate till the salt crystallises, redissolve in fresh water and acidify with hydrochloric acid.

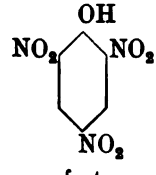
Properties.—Ortho. Yellow needles, characteristic smell. M.P. 45°; B.P. 214°. Easily volatile with steam; soluble in hot water, sparingly in cold.

Para. Should be colourless crystals (usually slightly yellow). M.P. 114°. Easily soluble in hot water, sparingly in cold.

(ii) *m-Nitrophenol.* This can be prepared by indirect means from benzene through *m*-dinitrobenzene (p. 359), *m*-nitraniline (p. 363), then diazotising the amino group as in the preparation of phenol from aniline (p. 367). Yellow crystals, M.P. 96°.

The nitrophenols give crystalline salts with alkali metals, and are far more strongly acidic than phenol as they dissolve in alkali carbonate solutions. (See p. 367.)

(iii) *Preparation of Picric Acid.*



(Schmitt, *B.* **2**, 52.)—

Dissolve 20 gms. of phenol in 20 gms. of strong sulphuric acid. Add this gradually to 120 gms. of strong nitric acid to which a little fuming nitric acid has been added. When all is added heat to 100° for 2 hours. Cool. Dilute with twice its volume of cold water, filter off the product at the pump, wash with a little cold water and recrystallise from hot water. Yield, 25 gms.

Properties.—1. Yellowish prismatic crystals. M.P. 122·5°. Explodes on detonating.

2. Dissolved in soda solution the sodium salt is obtained, which is a reagent for potassium and ammonium salts.

3. With benzene, naphthalene, anthracene, etc., in alcohol solution, beautifully crystalline compounds are obtained.

4. Some of the picrates, notably that of lead, are highly dangerous explosives.

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CHAPTER V.

REDUCTION OF NITRO-COMPOUNDS.

In the aromatic series, nitro-compounds form the starting-point for the preparation of many important nitrogen derivatives.

Reduction in neutral solution gives phenyl-hydroxylamine derivatives; in alkaline solution a hydrazo, -azo- or azoxy-body, in which two benzene nuclei are joined through a chain of two N atoms. Reduction in acid solution gives an amine. The preparations given are typical.

Reduction in neutral solution.

1. **Preparation of phenyl-hydroxylamine, $C_6H_5NH.OH$** (E. Fischer, *Org. Prep.*, 1905, 8).—Conduct the preparation in a fume-cupboard. Dissolve 10 gms. of ammonium chloride in 500 c.cs. of water and add 20 gms. of freshly-distilled nitro-benzene. Place the mixture in a large beaker surrounded by cold water. Stir with a mechanical stirrer and add gradually during ¾ hour, 25-30 gms. of 75 % zinc dust, keeping the temperature constantly between 14°-16°. When all odour of nitro-benzene has gone, filter the mixture on a Büchner funnel and wash the residue with 300 c.cs. of warm water sucked through very gently. The filtrate and washings are treated separately with 100 and 70 gms. of salt respectively, and the pptd. crystals filtered and pressed. Use for the preparation of nitroso-benzene.

Recrystallise a little from benzene for the tests.

Properties.—1. Colourless crystals. M.P. 81°. Soluble in water; very pungent odour, inducing sneezing.

2. Reduces Fehling's solution.

An alternative and better method (Wislicenus, *B.* **29**, 494) is to dissolve 1 part of nitro-benzene in 10 parts of ether, and add 1 part of freshly-made aluminium amalgam and 1 part of water. Leave for 10 minutes, filter, remove the ether and the body is thus obtained free from nitro-benzene and aniline. Recrystallise as before.

Reduction in alkaline solution.

2. **Preparation of azoxy-benzene,** $C_6H_5-N(\rightarrow O)-N-C_6H_5$ (Zinin, *J. pract. Ch.* (1) **36**, 98 (1845)).—Dissolve 20 gms. of clean sodium or 30 gms. of pure caustic soda in 200 gms. of methyl alcohol in a large flask with a reflux. Add

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30 gms. of nitro-benzene and heat on a boiling water-bath for 3-5 hours. If crystals of sodium formate settle out they may cause lumping; add a few glass capillaries if this occurs. Distil off most of the methyl alcohol on the water-bath and dilute the residue with water. Pour into a beaker and let it stand on ice. The liquid azoxy-benzene soon crystallises unless nitro-benzene is present, in which case the latter should be distilled off in steam.

Finally filter at the pump and press the crystals between filter-paper. Recrystallise from methyl alcohol or ligroin.

Properties.—Yellow crystals. M.P. 36°.

Löb performs the reduction electrolytically. (See *B.* **33**, 2332 (1900).)

3. **Preparation of azo-benzene** (Mitscherlich, *A.* **12**, 311).—Carefully dry 1 part of azoxy-benzene and 3 parts of coarse iron filings in a steam-oven. Grind together in a mortar and distil from a small non-tubulated retort. Heat *very gently* at first with a moving luminous flame. Gradually increase the heating till nothing further distils. Wash the distillate with hydrochloric acid, water, and press the crystals on a porous plate. Recrystallise from alcohol or ligroin.

Properties.—Red crystals. M.P. 68°; B.P. 295°.

4. **Preparation of hydrazo-benzene, $C_6H_5 . NH - NH . C_6H_5$.**—(i) May be made from nitro-benzene by reducing the alcoholic solution with zinc dust and caustic soda at a gentle boil. (Reflux.) Distil off the alcohol and separate from the zinc by carefully neutralising with dilute hydrochloric acid (Schultz).

(ii) It is more convenient however to use azo-benzene. Dissolve 5 gms. in 50 c.cs. of alcohol and add a solution of 2 gms. of caustic soda in 5 c.cs. of water in a flask fitted with a reflux. Boil and add about 8 gms. of zinc dust till the solution becomes colourless. Filter with suction, wash the residue with warm alcohol, and to the filtrate add sulphurous acid solution till turbidity appears. Cool, filter and recrystallise from ligroin with as little exposure to air as possible.

Properties.—1. Colourless plates. M.P. 126°.

2. Decomposes on heating into azo-benzene and aniline, becoming red.

3. In the presence of strong acid it undergoes a curious intramolecular change to **benzidene.**

$$C_6H_5 . NH - NH . C_6H_5 \longrightarrow NH_2 . C_6H_4 - C_6H_4 - NH_2.$$

A little hydrazo-benzene is covered with concentrated hydrochloric acid and allowed to remain for 5 minutes. Then treat with water, render alkaline with caustic soda and shake out the free benzidene with ether, three times. Unite the ethereal extracts, allow the ether to evaporate, and crystallise from hot water.

Properties.—1. Silvery leaflets. M.P. 122°.

2. If the aqueous solution be treated with dilute sulphuric acid the sulphate separates out.

5. **Reduction of one nitro group in a dinitro-body** (*Zinin's reaction*). *m-Nitraniline from m-dinitro-benzene* (Beilstein and Kurbatow, *A.* (1875) **176**, 44).—Dissolve 10 gms. of *m*-dinitro-benzene in 30 gms. of 90 % alcohol, and add 8 gms. of ·880 ammonia. Weigh and pass in hydrogen sulphide,

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then warm for 15 minutes with a reflux and repeat until there is an increase in weight of 6 gms. Add water to ppt. the product and filter. Dissolve the nitraniline in hydrochloric acid, and filter again from unchanged dinitrobenzene. Reppt. the filtrate with ammonia and recrystallise the ppt. from hot water.

Properties.—Long yellow needles. M.P. 116°; B.P. 285°.

Reaction:

$$4C_6H_4(NO_2)_2 + 6NH_4SH + H_2O = 4C_6H_4(NH_2)(NO_2) + 3(NH_4)_2S_2O_3.$$

Reduction in acid solution.

This is by far the most important reaction of the nitro-compounds, and yields the amino derivatives. The reducing agent is usually tin (or iron) and hydrochloric acid.

6. **Preparation of aniline, $C_6H_5NH_2$.**

Reaction:

$$C_6H_5NO_2 + Sn + 4HCl = C_6H_5NH_2 + SnCl_4 + 2H_2O.$$

$$C_6H_5NH_2 + HCl = C_6H_5NH_3Cl.$$

$$2C_6H_5NH_3Cl + SnCl_4 = (C_6H_5NH_3)_2SnCl_6.$$

$$(C_6H_5NH_3)_2SnCl_6 + 10NaOH = 2C_6H_5NH_2 + NaCl + Sn(ONa)_4 + 6H_2O.$$

In a 1½ litre round-bottomed flask put 80 gms. of granulated tin and 40 gms. of nitro-benzene. Fit with a tube 70 cms. long and 1·5 cms. diameter to act as a reflux condenser. Through this tube add 200 c.cs. of concentrated hydrochloric acid in quantities of about 10 c.cs. at a time. (If the reaction mixture boils actively aniline will be lost. At the least sign of boiling immerse the flask in cold water.) Shake well after each addition of acid. Finally heat on the water-bath for an hour without the condenser. Meanwhile prepare a solution of 150 gms. of caustic soda (commercial lumps) in 200 c.cs. of water.

Fit up an apparatus for distilling in steam (from the reaction flask). When all is ready and the water boiling, add the soda carefully to the reaction mixture (do not allow to boil) and then distil in steam till 50 c.cs. have passed over after the drops falling from the condenser are no longer turbid. Saturate the distillate with salt and extract with ether. Dehydrate the extract with solid caustic soda and distil off the ether. Rectify the aniline (air condenser). Yield almost theoretical.

Properties.—1. Liquid, colourless when freshly distilled, turning yellow and finally dark brown on keeping. Characteristic smell. B.P. 182°; S.G. 1·026 at 15°. Soluble in ether, soluble to about 3 % in water.

2. Strong hydrochloric acid ppts. the hydrochloride, readily soluble in water.

3. Dilute solutions of *free* aniline give a purple coloration with bleaching-powder solution.

4. Bromine water ppts. tribromaniline.

5. One drop of aniline, a drop of chloroform, and 1 c.c. of alcoholic potash give, on warming, an intense and disagreeable odour of $C_6H_5 . N . C$. (Do in draught-cupboard and pour away at once. (See under Chloroform, p. 305.)

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6. To aniline hydrochloride in excess of acid add sodium nitrite. A diazo salt is formed, which on warming decomposes with evolution of nitrogen and phenol is left.

7. Dissolve 1 drop of aniline in 1 c.c. of strong sulphuric acid, stir and add a few drops of potassium dichromate. A fine blue colour is obtained.

In a like manner any amine may be obtained from the corresponding nitro-body.

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CHAPTER VI.

DIAZO COMPOUNDS AND THEIR REACTIONS.

WHEN aniline salts are treated at 0° with nitrous acid the diazo reaction ensues.

$$C_6H_5 . NH_3Cl + O : N . OH = C_6H_5\underset{\underset{N}{\|}}{N} . Cl + H_2O.$$

This substance is called diazonium chloride (diazo-benzene chloride). If isolated they are dangerously explosive when dry. In solution they are very reactive and the diazo grouping may be replaced by, or coupled with, a large variety of radicals.

1. **Preparation of diazo-benzene chloride.**—15 gms. of pure aniline hydrochloride are suspended in 45 gms. of glacial acetic acid. Cool the vessel with ice and add gradually, with constant stirring, slightly more than the theoretical amount of amyl nitrite. The undissolved aniline salt disappears, and the reaction is complete when a test portion treated with sodium acetate no longer gives a yellow diazo-amino compound. By treatment with ether the crystalline hydrochloride is pptd. and may be filtered at the pump. On no account dry it, except in small quantities, as it is very explosive.

2. **Preparation of diazo-benzene sulphate.**—As above, with 10 gms. of aniline in 100 gms. of pure alcohol, and adding 20 gms. of strong sulphuric acid. 12 gms. of amyl nitrite cause the required sulphate to crystallise out. Filter and wash with alcohol. Explosive when dry.

REACTIONS OF THE DIAZO GROUP.

A. Replacement.

1. **By hydrogen. Preparation of a hydrocarbon from an amine.**—Various methods are available.

(*a*) *By treatment with alcohol. m-nitro-toluene from nitro-toluidine.*—Dissolve 1 part of nitro-toluidine in 3 parts of alcohol and add carefully 3 parts of strong sulphuric acid, in a tall beaker. Cool with ice and add the theoretical quantity of sodium nitrite dissolved in the minimum of water. This solution is added through a thistle-funnel so that it goes to the bottom of the liquid before the nitrous acid is set free. Small quantities at a time are added with constant stirring till a test portion shows free nitrous acid with starch-iodide paper.

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Warm on a water-bath till no more nitrogen is evolved, distil off the alcohol, dry the product with calcium chloride and rectify. B.P. 230°.

(*b*) *By alkaline stannite. Benzene from aniline, toluene from toluidine, etc.*—Dissolve 1 part of the amine in 3 parts of strong hydrochloric acid and 5 parts of water. Cool with ice and treat as previously described with 1 part of sodium nitrite in 3 parts of water till free nitrous acid is recognised. Now pour the solution into about half its volume of 30 % caustic soda. The stannite solution (prepared by dissolving 4 parts of stannous chloride in 10 of water, and adding to it 60 % caustic soda solution till the ppt. first formed is redissolved) is now added to the alkaline diazo solution, a little at a time, cooling with ice. Shake after adding each portion and wait till the evolution of nitrogen ceases before adding the next.

The product may be steam distilled, ether extracted, etc., for the isolation of the hydrocarbon.

Replacement by hydroxyl.

2. **Phenol from aniline.**—To the hot solution made by pouring quickly 30 gms. of sulphuric acid into 80 c.cs. of water and stirring, add carefully 15 gms. of aniline and then 120 c.cs. of water. Cool, diazotise as before with 14 gms. of sodium nitrite in 60 c.cs. of water, till free nitrous acid is detected. Distil off the phenol in a current of steam after heating for half an hour on the water-bath. Salt out the distillate, extract with several portions of ether, dry the combined extracts with fused sodium sulphate and fractionate with an air-condenser for the phenol.

Properties.—1. Colourless crystals. M.P. 43°; B.P. 183°. Characteristic smell; somewhat soluble in cold water, miscible with hot water.

2. It dissolves in alkalis forming "phenates," but *not* in alkali carbonates. Phenol is often termed "carbolic acid" from its acidic nature.

3. Bromine water ppts. *sym*-tribromo-phenol as a pale yellow ppt. when added to a solution of phenol.

4. Ferric chloride gives a violet colour, destroyed by acids.

Note.—*All* phenols give some coloration with ferric chloride.

5. Ammonia, followed by a few drops of hypochlorite solution gives a blue colour on warming.

6. **Liebermann's reaction.**—To phenol add strong sulphuric acid in which some solid potassium nitrite has been dissolved. A green colour is obtained, turning red on dilution and blue on adding alkali. (Other phenols give this reaction.)

3. **Hydroquinone from *p*-amino-phenol** (Griess, *A.* **137**, 67).—21·6 gms. of *p*-amino-phenol are diazotised as before (*sulphuric acid*), and the solution digested with a boiling solution of 100 gms. of copper sulphate in 700 c.cs. of water. Extract the hydroquinone with ether and crystallise.

Replacement by chlorine, bromine and cyanogen.

Sandmeyer showed that when a diazo salt was heated with the corresponding cuprous salt, the acid radical in question takes the place of the diazo group. The action of the cuprous salt is not understood. (Sandmeyer, *B.* **17**, 2650; **20**, 1495.)

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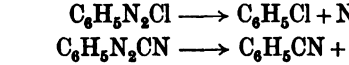
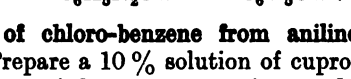
Gattermann showed that in some cases the required acid and freshly-reduced copper powder acted in a similar way.



$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2.$$



$$C_6H_5N_2CN \longrightarrow C_6H_5CN + N_2.$$

4. **Preparation of chloro-benzene from aniline. *p*-Chloro-toluene from *p*-toluidine, etc.**—Prepare a 10 % solution of cuprous chloride from 4 gms. of copper oxide, 15 gms. of fine copper turnings and 100 c.cs. of strong hydrochloric acid. Boil in a flask till colourless. Place the solution in a litre flask fitted with a reflux and boil, then add slowly through the condenser the solution obtained by diazotising 20 gms. of aniline in 50 c.cs. of strong hydrochloric acid and 50 c.cs. of water, with 17 gms. of sodium nitrite in 50 c.cs. of water. (See above.) Shake vigorously after each addition. When complete, distil in steam. Add a little caustic soda to the distillate to fix any phenol, separate the lower layer of chloro-benzene, dry with calcium chloride and rectify. B.P. 132°. *p*-Chloro-toluene boils at 162°. M.P. 7·4°.

Bromo-benzene, etc., are prepared similarly, using the diazo-*sulphate* to prevent the formation of any chloro-body, and a solution of cuprous bromide *or* hydrobromic acid and copper *powder*.

Quantities required.—20 gms. of aniline, 100 c.cs. of water, 20 c.cs. of strong sulphuric acid, diazotised as above. This is added to cuprous bromide made from 20 gms. of copper sulphate crystals, 57 gms. of potassium bromide, 120 c.cs. of water, 15 gms. of fine copper turnings and 4-5 c.cs. of strong sulphuric acid, boiled till colourless. Use 100 c.cs. of the resulting solution.

B.P. of bromobenzene, 155°; S.G. 1·5.

5. **Preparation of phenyl cyanide (benzonitrile).**—Dissolve 50 gms. of crystallised copper sulphate in 200 c.cs. of warm water in a litre flask on a water-bath in an *efficient* fume-cupboard. Add gradually, with continuous shaking, a solution of 55 gms. of potassium cyanide in 100 c.cs. of water from a tap-funnel. Cyanogen is copiously evolved. (On no account breathe any of it !) Warm the product to 65°-70° on a water-bath and add gradually a diazotised aniline solution (20 gms. of aniline) prepared as before. Shake after each addition, and when all is added (10 minutes) heat on the water-bath for 15 minutes and distil in steam in the draught-cupboard. Extract the distillate with ether, wash the extract with dilute caustic soda to separate any phenol, then with dilute sulphuric acid. Dry the extract over potassium carbonate, distil off the ether and fractionate.

***p*-Tolyl cyanide** may be similarly prepared from *p*-toluidine. It is simply filtered from the steam-distillate and dried between filter-paper, then distilled.

Properties.

Benzonitrile.—1. Colourless liquid (usually somewhat yellow). B.P. 191°.

Toluonitrile.—1. Crystalline solid. M.P. 38°; B.P. 218°.

2. Both are readily hydrolysed to their respective acids by boiling with mineral acid. (See p. 384.)

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Gattermann's modification of Sandmeyer's reaction.

6. **Preparation of chloro-benzene, etc.** (Gattermann, *B.* **23**, 1218; **25**, 1086).—Copper powder, prepared by the action of zinc dust on copper sulphate solution and washed with dilute sulphuric acid then water, is added gradually to a diazonium chloride prepared as before. Heat on a water-bath with reflux, finally steam distil and purify as before.

Chloro-benzene. (from aniline)	B.P. 132°.	*p*-Chloro-toluene. (from *p*-toluidine)	B.P. 163°.

Replacement by iodine.

7. **Preparation of iodo-benzene, C_6H_5I.**—This is done very simply by the action of potassium iodide on the diazonium salt. (Griess, *A.* (1866), **137**, 76.)

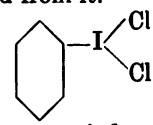
Prepare diazonium chloride or sulphate solution from 20 gms. of aniline as before. Pour it into a solution of 40 gms. of potassium iodide in 100 c.cs. of water. Heat on a water-bath (reflux) till no more nitrogen is evolved, steam distil the product, extract with ether and wash the extract with (*a*) water, (*b*) caustic soda solution to remove free iodine, (*c*) water, then dry over calcium chloride and rectify.

Properties.—1. Heavy yellow liquid. B.P. 190°; S.G. 1·84 at 15° C. Insoluble in water.

2. Dissolved in chloroform and treated with chlorine, fine yellow crystals (needles) of $C_6H_5ICl_2$ are obtained. See next preparation.

Derivatives of iodo-benzene (Willgerodt, *J. pr.* [2], **33**, 155).—Iodo-benzene is notable from the extreme readiness of the iodine to assume the trivalent state. The following compounds are prepared from it.

8. **Preparation of iodo-benzene dichloride.**

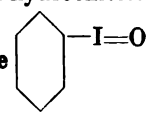


Dissolve 20 gms. of iodo-benzene in 50 gms. of dry chloroform. Pass in a stream of dry chlorine using an inverted funnel just dipping into the solution as a delivery tube. In a few minutes yellow crystals separate. When there is no further action, filter, wash with a little chloroform, spread out on filter-paper and allow to dry.

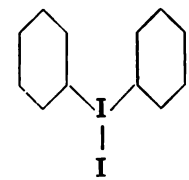
Properties.—1. Yellow needles; unstable; evolve chlorine at 80°; at 120° decomposition is complete.

2. If kept in a bottle, chlorine enters the nucleus, displacing hydrogen, and on opening the bottle fumes of hydrochloric acid emerge.

9. **Preparation of Iodoso-benzene**



and diphenyl iodonium iodide



—Rub together in a mortar 5 gms. of iodo-benzene dichloride with 20 gms. of

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10 % caustic soda solution. Leave for several hours. The white insoluble mass is filtered, washed and pressed (iodoso-benzene). The filtrate, which contains the iodide, is saturated with sulphur dioxide. The ppt. obtained is recrystallised from hot water (diphenyl iodonium iodide).

Properties.

Iodoso-benzene.—1. Puffs up and decomposes when heated to 210°.

2. Treated with acids it forms salts, *e.g.* dissolve in the minimum of glacial acetic acid, evaporate and recrystallise from benzene.

$$C_6H_5I(CO_2CH_3)_2.$$

Diphenyl iodonium iodide.—1. Colourless needles.

2. When heated it is converted into iodo-benzene.

3. Treated with freshly-pptd. silver oxide the free base is obtained, though its actual preparation by another method is more convenient (see below). This remarkable substance,

$$\begin{array}{c} C_6H_5—I—C_6H_5 \\ | \\ OH \end{array}$$

is a base of the order of ammonium hydroxide.

10. **Preparation of iodoxy-benzene, $C_6H_5IO_2$** (Willgerodt, *B.* **25**, 3500; **26**, 358, 1310).—This compound (also called phenyl iodite) is made by distilling in steam a thin paste of iodoso-benzene and water.

When no more iodo-benzene comes over, evaporate the residue in the distilling-flask on a water-bath and cool. The crystals which separate are filtered. Recrystallise from water.

Properties.—1. On heating, puffs up suddenly and decomposes. The substance explodes at 230° (care !).

2. It has no basic properties.

3. Mixed with an equi-molecular proportion of iodoso-benzene and treated with freshly-pptd. silver oxide, diphenyl iodonium hydroxide is obtained.

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2 : I . OH + AgIO_3.$$

11. **Reduction of diazo-benzene to phenyl hydrazine, $C_6H_5NH-NH_2$** (Meyer, *B.* **16**, 2976).—The reduction in *acid* solution is carried out by stannous chloride.

Diazotise as usual 20 gms. of *freshly-distilled* aniline in 60 gms. of hydrochloric acid and 150 c.cs. of water. Saturate with 60 gms. of salt, with thorough shaking. Pour off from any undissolved salt and cool with ice. Add a solution of 120 gms. of stannous chloride in 50 gms. of strong hydrochloric acid and leave overnight. Filter off the phenyl-hydrazine hydrochloride on a Büchner funnel, press it out, and if the free base is required, decompose it by adding it to excess of caustic soda solution. Extract the oil with ether, dry the extract with potassium carbonate and distil off the ether. Then distil the base *in vacuo*. Yield, 20 gms. B.P. 120° at 12 mm. pressure.

Properties.—1. Colourless oil when freshly made. Rapidly discolours. M.P. 23°; B.P. 240° (about).

2. Strongly basic. Forms salts.

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3. Condenses with aldehyds and ketones forming hydrazones, and with sugars forming osazones (*q.v.*).

4. Powerful reducing agent (Fehling, etc.).

Other reactions of diazonium salts.

Note.—Bamberger has shown that diazonium salts exist in two forms, one much more active than the other. He formulates the active form (which performs the reactions described in this chapter) as

$$C_6H_5-\underset{\underset{N}{\|}}{N}-Cl, \text{ and the inactive form as } C_6H_5 . N = N . Cl.$$

Hantzsch shows that the latter exists in two modifications (geometrical isomers) and in some cases has isolated both forms, *cis* and *trans*.

12. **Preparation of diazonium perbromide.**

$$C_6H_5N_2Br + Br_2 = C_6H_5N_2Br_3.$$

Diazotise a few c.cs. of aniline in the usual way. To it add an equal volume of bromine dissolved in strong potassium bromide solution. Separate the oil which forms, wash it with water and allow to stand. After a time it crystallises.

13. **Preparation of diazo-amino-benzene,** and its conversion to **amino-azo-benzene** (Gattermann, *A.* **121**, 257).

$$C_6H_5N_2Cl + C_6H_5NH_2 = C_6H_5N_2 . NHC_6H_5.$$

Diazotise 10 gms. of aniline in 100 c.cs. of water and 35 gms. of hydrochloric acid of S.G. 1·185 (12 gms. of anhydrous HCl) with 8 gms. of sodium nitrite. Have ready a solution of 10 gms. of aniline in the theoretical quantity of dilute hydrochloric acid. Cool it to 0° and add it to the diazonium salt, also at 0°. Now add an ice-cold solution of 50 gms. of sodium acetate in the minimum of water and set aside for half an hour. Filter off the product on the pump, wash with water, press and crystallise from ligroin or alcohol. Yield, theoretical.

Properties—1. Yellow plates. M.P. 96°-98°. Insoluble in water. Explodes at 100°.

2. In alcohol solution it gives, on addition of alcoholic silver nitrate, a red crystalline ppt. of $C_6H_5 . N_2 . NAg . C_6H_5$.

3. It undergoes an intramolecular change to amino-azo-benzene (see next preparation).

14. **Preparation of amino-azo-benzene, $C_6H_5 . N_2 . C_6H_5 . NH_2$** (Gattermann, *B.* **10**, 1309; **20**, 372, 904).—Prepare a few gms. of aniline hydrochloride by adding strong hydrochloric acid to 4 gms. of aniline, filtering by suction and pressing the ppt. between filter-paper.

Mix 4 gms. of this with 8 gms. of powdered diazo-amino-benzene and 20 gms. of freshly-distilled aniline. Heat for an hour on a water-bath at 40°-45°. Allow to stand for several hours and then add hydrochloric acid (1 : 1) in excess, not allowing the temperature to rise above 70°. The hydrochloride separates and is washed with dilute hydrochloric acid to dissolve any aniline hydrochloride.

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To obtain the free base, warm the hydrochloride with dilute ammonia, filter off the product, dissolve it in alcohol containing a few drops of ammonia and add hot water till turbidity appears. On cooling, orange prisms, M.P. 127°, separate.

Condensations or "coupling" reactions of diazonium salts with sulphonic acids, amines and phenols will be dealt with later.

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CHAPTER VII.

SOME OTHER AMINE DERIVATIVES.

ANILINE, etc., salts are obtained as solids by the direct action of cold concentrated acid on the base. They crystallise well from water. On adding chlorplatinic acid to their hydrochloride solutions, a yellow crystalline ppt. forms, precisely analogous to the corresponding ammonium salt. This reaction is used for finding the molecular weight of the base.

Derivatives in which the hydrogen of the amino group is replaced.

1. **Preparation of acetanilide, $C_6H_5 . NH . CO . CH_3$** (Williams, *J.C.S.*, 1864, 106).

(*a*) In a round-bottomed 250 c.cs. flask, connected with a long wide upright tube to act as an air-cooled reflux, heat a mixture of 25 gms. of aniline and 30 gms. of glacial acetic acid for 7-8 hours on a sand-bath. Whilst hot pour into 500 c.cs. of cold water. Filter on the pump and wash with a little cold water. Recrystallise by boiling with water containing a little alcohol, filter whilst hot and set aside. The solution may be decolorised first if necessary by boiling with animal charcoal. Yield, 30-35 gms.

Properties.—1. White rhombic plates. M.P. 114°; B.P. 295°. Sparingly soluble in water.

2. Hydrolysed to aniline (hydrochloride) and acetic acid by boiling with strong hydrochloric acid.

3. *p*-Bromacetanilide is obtained (Remmers, *B.* (1874) 346) by dissolving 4 gms. in 20 c.cs. of glacial acetic acid and adding 5 gms. of bromine in 6 c.cs. of glacial acetic acid. Stand aside for 15 minutes and pour into excess of cold water.

Recrystallise the washed crystalline ppt. from alcohol.

4. Employed as a febrifuge (" anti-febrin ").

(*b*) Alternatively (Franzen, *B.* (1909) **42**, 2465) the action of acetyl chloride or acetic anhydride on 1^{ry} and 2^{ry} amines yields the acetyl derivative. Simply warm the two bodies together for a few minutes and pour into water to decompose the excess of anhydride.

2. **Preparation of 2^{ry} and 3^{ry} amines and derivatives.**

(i) *Methylaniline*, $C_6H_5 . NH . CH_3$ (Hepp, *B.* (1877) **10**, 327).—Heat 15 gms. of acetanilide, 4 gms. of sodium (best as wire) and 75 gms. of xylene (as solvent) in a flask with a reflux, for 2-3 hours at 130° (oil-bath). Cool, add 16 gms. of methyl iodide and warm till no more methyl iodide comes

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off. Distil off the xylene and boil with concentrated potash solution for 24 hours (reflux). Acidify with hydrochloric acid, distil in steam to remove any remaining xylene, etc.; again render alkaline and distil off the methyl aniline in steam. Extract the distillate with ether, dry with solid potash and fractionate. B.P. 192°.

Properties.—1. Liquid, strong aromatic odour. S.G. 0·975.

2. Bleaching-powder solution gives a violet colour, changing to brown.

3. Nitrous acid forms a nitrosamine, a yellow oil with no basic properties, which on treatment with phenol dissolved in strong sulphuric acid, dilution with water and making alkaline with potash gives an intense blue colour. (Liebermann's reaction for nitrosamines.)

(ii) *Dimethylaniline*, $C_6H_5N(CH_3)_2$ (Walter, *Chem. Zeit.*, 1910, **34**, 641, etc.).

(*a*) 80 gms. of aniline, 78 gms. of *pure* methyl alcohol and 8 gms. of sulphuric acid are heated in a small autoclave (a steel vessel with enamel lining and a screw-on lid, to withstand high pressures) for 2 hours to 150° and for 6 hours to 180°. Considerable pressure is developed (up to 25 atmospheres on the large scale). The contents after cooling are made alkaline with caustic soda and steam-distilled. Separate the oil, dry with potash and fractionate. B.P. 190°-200°.

(*b*) If an autoclave is not available, use 20 gms. of aniline hydrochloride, 15 gms. of aniline and 22 gms. of pure methyl alcohol. Heat together in a bomb-tube (see p. 417) for 2 hours to 150° and for 6 hours to 190°. Pour the whole contents of the tube, after opening, into a separating funnel, add excess of caustic soda and shake. Add some ether, remove the top layer, and extract the lower aqueous layer twice more with ether. The united ethereal solutions are dried over potash, filtered, the ether distilled off and unchanged aniline converted to acetanilide by boiling with 25 gms. of acetic anhydride (reflux) for an hour. Then distil and fractionate.

(*c*) *Nölting's* method (B. **24**, 563), which is more convenient, is to treat aniline, etc., with rather more than the theoretical amount of methyl iodide and excess of sodium carbonate solution. Heat on a water-bath (reflux) for 2 hours. Render alkaline with caustic soda, extract with ether, dry over solid potash and fractionate.

Properties.—1. Colourless liquid. Characteristic disagreeable odour. B.P. 190°-200°. Darkens readily like aniline.

2. Warmed with methyl iodide a crystalline quaternary ammonium iodide is obtained.

3. With nitrous acid an intense green product, *p*-nitrosodimethyl aniline, is obtained. See next preparation.

(iii) *p*-**Nitrosodimethyl aniline** (Baeyer, Caro, *B.* **7**, 963).—20 gms. of aniline are dissolved in 50 c.cs. of strong hydrochloric acid and 100 c.cs. of water added. Run in slowly a solution of 12 gms. of sodium nitrite, below 8°, with constant stirring. Leave for an hour. Filter off the pptd. hydrochloride, wash with methylated spirit containing hydrochloric acid, and if the free base is required dissolve in water and treat with potassium carbonate. Shake out with ether and allow the extract to evaporate.

Properties.—1. Large green leaflets. M.P. 85°.

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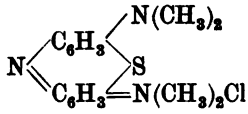
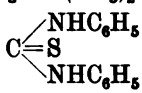
2. Solution in hydrochloric acid is decolorised by zinc dust owing to reduction to dimethyl *p*-phenylene diamine.

$$(CH_3)_2 : N . C_6H_4 . NO = (CH_3)_2 : N . C_6H_4 . NH_2.$$

3. Warm some of the crystals of *p*-nitrosodimethyl aniline with ammonium sulphide. Acidify with hydrochloric acid and add ferric chloride. Methylene blue is produced.



(iv) **Thiocarbanilide.**



Heat together on a water-bath, in a flask fitted with a reflux, 4 parts each of alcohol, carbon disulphide and aniline and 3 parts of potash. Then distil off the carbon disulphide and alcohol, and add water to the residue. Filter the crystals which separate, wash with dilute hydrochloric acid to remove any aniline, then with water. The crude product may be used for preparations, but it may be crystallised from alcohol if wanted pure.

Properties.—1. Colourless rhombic tablets. M.P. 154°. Soluble in alcohol and ether.

2. Forms isothiocyanates. See next preparation.

(v) **Phenyl isothiocyanate** (phenyl mustard oil), $C_6H_5N : C : S$ (Weith, Merz, *Z.* 1869, 589).—Distil a mixture of 1 part of thiocarbanilide with 5 parts of strong hydrochloric acid (fume-cupboard) till about 15 c.cs. only remain (see below). Extract the distillate with ether, dry, remove the ether and rectify.

Properties.—1. Colourless oil. B.P. 220°.

2. Heated with aniline, thiocarbanilide is formed.

3. Heated with yellow mercuric oxide the sulphur is replaced by oxygen.

Note.—The residue left in the flask above is the hydrochloride of tri-phenyl guanidine. If sufficiently concentrated it will crystallise on cooling. Wash on the filter with a little water and warm gently with dilute caustic soda. The free base is obtained and may be recrystallised from alcohol. The crystals are needle-shaped. M.P. 143°. Feeble base.

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CHAPTER VIII.

PHENOLS AND THEIR DERIVATIVES.

1. **Preparation of phenol from benzene sulphonic acid.**

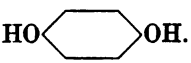
$$C_6H_5SO_3K + KOH = K_2SO_3 + C_6H_5OH.$$

Dissolve 40 gms. of caustic potash (not soda) in very little water and heat gently in an iron or nickel basin. (*Care of eyes and hands!*). Add gradually with constant stirring 20 gms. of potassium benzene sulphonate. Keep the temperature about 240°. After an hour pour out the molten mass on to a clean tile, dissolve in water, acidify with strong hydrochloric acid and repeatedly extract with ether. Dehydrate the extracts with potassium carbonate, distil off the ether and then the phenol. B.P. 180°. (Reactions on p. 367.)

Similarly make catechol from potassium *o*-phenol sulphonate, and resorcinol from sodium *m*-benzene disulphonate.

2. **Preparation of ethers.** *Anisol*, $C_6H_5.OCH_3$; *Phenetol*, $C_6H_5.OC_2H_5$ (Cahours, *Ann.* (1851) **78**, 226).—A 250 c.cs. round-bottomed flask is fitted with a reflux and 100 c.cs. of methyl (or ethyl, according to the preparation) alcohol poured in. 4·6 gms. of sodium are then added in small pieces, and when dissolved, cool and add the theoretical quantities of phenol and the required iodide. (18·8 gms. of phenol, 32 gms. of methyl iodide or 35 of ethyl iodide). Heat on a water-bath for 3 hours (till the alkaline reaction disappears). Distil off as much alcohol and unchanged iodide as possible from the water-bath, treat the residue with water, separate the oil with ether and dehydrate over calcium chloride. Distil off the ether and rectify the residue.

Properties.—Colourless stable liquids. Agreeable smell. B.P. of anisol, 152°; of phenetol, 172°.

3. **Preparation of quinol. (Hydroquinone)** 

Best prepared from quinone (*q.v.*) by saturating the aqueous solution with sulphur dioxide, allowing to stand for some time, extracting with ether and allowing the extract to evaporate. Recrystallise from dilute sulphur dioxide solution.

Properties.—1. Colourless prisms. M.P. 169°. Soluble in the usual solvents.

2. Ferric chloride turns the solution brown. Quinone may be extracted from this by ether.

3. Reduces Fehling's solution.

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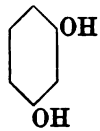
4. Reduces silver salts in alkaline solution. It is used as a photographic developer on this account.

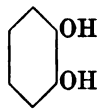
Properties of Resorcinol.



M.P. 119°

1. Can be distinguished from hydroquinone and catechol by the formation of fluorescein when heated gently with phthalic anhydride and zinc chloride. The brown melt is dissolved in caustic soda and poured into much water. Fine greenish yellow fluorescence. (See Chap. XIII.)
2. Ferric chloride produces a violet colour.
3. Bromine water ppts. tri-bromoresorcinol.
4. Reduces Fehling's solution and alkaline silver solutions.

Properties of Catechol.



M.P. 104°

1. Ferric chloride gives a green coloration, turning red on adding sodium carbonate. (This is characteristic of *o*-diphenols.)
2. It is a reducing agent similar to the others.

4. **Preparation of pyrogallol (pyrogallic acid) $C_6H_3(OH)_3$.**

(1. 2. 3. **trihydroxybenzene) from gallic acid** (Liebig, *A.* **101**, 48). Fix up a retort through the tubulus of which a stream of CO_2 can be passed. In the retort place a mixture of two parts of powdered pumice with one part of gallic acid, and attach a receiver to the end of the retort.

Pass CO_2 and heat. After a while, pyrogallol collects in the form of needles in the neck of the retort from which it may be melted into the receiver.

Properties.—1. Very light needles. M.P. 132-3°. Very soluble in water, alcohol and ether.

2. In alkaline solution, it darkens in air owing to absorption of oxygen; hence its use in quantitative oxygen estimations.

3. In alkaline solution, it is a powerful reducing agent, giving a black ppt. of silver from ammoniacal silver oxide; hence its use as a photographic developer.

4. Ferric chloride gives a red colour; $FeSO_4$ a dark blue colour.

Properties of phloroglucinol, 1. 3. 5. trihydroxybenzene.

1. White crystalline solid. M.P. 218°. Soluble in water.
2. Ferric chloride gives a blue coloration.
3. Its solution in HCl (sp. gr. 1·15) gives a red colour on boiling with pentoses. (See p. 409.)

Properties of gallic acid, 2. 3. 4. trihydroxybenzoic acid.

1. White crystalline solid. M.P. 230-240°. Soluble in hot, slightly in cold water.
2. Its alkaline solution darkens with alkalis.
3. Ferric chloride gives a dark blue ppt. (basis of ink).

Tannic acid or *tannin*, $C_{27}H_{22}O_{17}$ is related to gallic acid, and gives similar reactions, except that it is very soluble and gives ppts. at once with $CuSO_4$ and gelatine.

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CHAPTER IX.

SOME OXIDATIONS AND REDUCTIONS.

THE following oxidations will now be dealt with :

Side-chain to carboxyl.
Amine, etc., to quinone.
Hydroxylamine derivative to nitroso-body.

And the following reductions :

Ketone to hydrocarbon.
Phenol to hydrocarbon.
Cinnamic acid to hydrocinnamic acid.

A. OXIDATIONS.

1. **Toluene (benzyl chloride, etc.) to benzoic acid.**—Strong nitric acid, chromic acid, permanganate, etc., are all employed as side-chain oxidising agents. It is sometimes more convenient to employ a halogenated side-chain derivative, which is easier to oxidise.

(*a*) Boil 12 gms. of toluene with 40 gms. of potassium dichromate, 55 gms. of sulphuric acid, and 80 c.cs. of water in a flask with a reflux till the toluene has disappeared. Cool, filter and recrystallise the benzoic acid from hot water.

(*b*) In a flask fitted with a reflux put 5 gms. of benzyl chloride, 4 gms. of anhydrous sodium carbonate and 50 c.cs. of water. Add gradually 9 gms. of permanganate in 150 c.cs. of water. Boil for 2-3 hours on a wire gauze; pass in sulphur dioxide till the ppt. of manganese dioxide dissolves. Cool, filter and recrystallise from hot water.

Properties.—1. White plates with a pearly lustre. M.P. 121°. Volatile in steam. Soluble in hot water, alcohol and ether. The vapour has a characteristic smell.

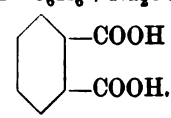
2. Ferric chloride ppts. buff basic ferric benzoate from neutral solutions.

3. Silver nitrate ppts. white silver benzoate from not too dilute neutral solutions.

4. Heated with soda-lime, benzene is evolved.

$$C_6H_5 . COONa + NaOH = C_6H_6 + Na_2CO_3.$$

2. **Naphthalene to Phthalic acid**



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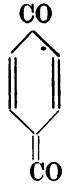
35 gms. of naphthalene are dissolved in 470 gms. of fuming sulphuric acid (containing 6-7 % of anhydride) with constant stirring. 18 gms. of mercuric sulphate are added, and the whole placed in a tubulated retort fitted with a thermometer and a cooled receiver (condenser unnecessary), and carefully heated. Oxidation begins at 200° and at 250° a mixture of sulphuric acid and phthalic anhydride distils. Continue till the residue is practically solid. Drain the distillate from sulphuric acid as far as possible, and add to some water, boil and cool. Filter off the phthalic acid, wash with a little cold water and recrystallise from boiling water.

Properties.—1. Short white prisms. M.P. 213°.

2. Heated slowly it gives off water and the anhydride sublimes as white needles, M.P. 128°. The latter may be prepared in quantity from the acid by heating in a subliming apparatus or distilling carefully from a retort, rejecting the water which comes over first. It is used in preparing phthaleïns.

3. Heated with soda-lime, benzene is evolved.

3. **Aniline to Quinone.**  :— ***o*-Toluidine to toluquinone.**

Many *p*-derivatives of benzene can be oxidised to quinone, but it is also readily obtained from aniline, etc. Dissolve 20 gms. of aniline (or *o*-toluidine) in 600 c.cs. of water and 95 c.cs. of sulphuric acid. Place in a large beaker, cool with ice and stir (best with a turbine) during the whole time that 60 gms. of powdered sodium dichromate are being added, 1 gm. at a time. This should take an hour. Leave overnight, and treat in one of the following ways.

(*a*) Extract three times with 300 c.cs. of ether each time. *Do not shake vigorously or the ether will not separate.* (Distil the ether off and use again.) Finally the ethereal extract is freed from ether in a large flask, and the crystalline mass is steam-distilled, the distillate extracted with ether, evaporated and dried. Yield, 15 gms.

(*b*) Reduce to hydroquinone by saturating with sulphur dioxide from a syphon of the liquid gas. The hydroquinone may then be ether-extracted without difficulty. The hydroquinone, after evaporation of the ether, is reoxidised with dichromate or ferric chloride and the quinone steam-distilled. Purify as before.

Properties.—1. Orange yellow needles, M.P. 116° (toluquinone, M.P. 67°). All *p*-quinones have a similar characteristic pungent odour.

2. Easily reduced to hydroquinones.

3. Form additive bodies with bromine, hydroquinone, phenol, etc., when the warm petrol solutions are mixed and cooled. Phenoquinone forms fine deep red crystals.

4. **Hydroxylamine derivative to nitroso-compound.** *Nitroso-benzene from phenyl hydroxylamine* (Bamberger, *B.* **28**, 1221).—An ice-cooled solution of 4·6 gms. of potassium dichromate is added quickly to a freshly-made ice-cooled

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solution of 4 gms. of phenyl hydroxylamine in 270 c.cs. of water and 30 gms. strong sulphuric acid. A steam boiler being ready at the boil, and the rest of the apparatus prepared, the product is distilled in steam without delay. Deep green oily drops come over, changing to nearly colourless crystals in the receiver. Filter and press them out on a porous plate, then wash with petrol.

Properties.—Colourless crystals, melting at 67°·5 to a deep green liquid. Piercing odour.

The above colour change on melting (or solidifying) is characteristic of nitroso-bodies.

B. REDUCTIONS.

1. **Aromatic ketone to hydrocarbon** (Coombes, *J.C.S.*, 1887, 1424). *Benzophenone to diphenyl methane.*

(*a*) *By hydriodic acid.*—Heat a mixture of 5 gms. of benzophenone, 6 gms. of hydriodic acid (B.P. 127°) and 1 gm. of red phosphorus in a Carius bomb-tube (*q.v.*) for 6 hours at 160°. Extract the product repeatedly with ether, and fractionate after distilling off the ether. B.P. 263°. M.P. 27°.

(*b*) *By sodium amalgam.*—20 gms. of benzophenone in 200 c.cs. of absolute alcohol are treated gradually with 400 gms. of 2 % sodium amalgam whilst the whole is boiled gently on the water-bath (reflux). Separate from the mercury, neutralise exactly with sulphuric acid, distil off the alcohol, and rectify the residue as before.

2. *Phenol to hydrocarbon.*—This is readily carried out by mixing with zinc dust and distilling dry. All phenols are thus converted to their corresponding hydrocarbons.

See also anthracene from anthraquinone.

3. **Reduction of unsaturated to saturated body.** *Cinnamic acid to hydrocinnamic acid.*—Make a solution of 10 gms. of cinnamic acid in exactly the correct amount of dilute caustic soda. Keep at 30°-35° on a water-bath and treat with 200 gms. of 2 % sodium amalgam added in small portions, shaking well after each addition. As the action proceeds the mixture is kept approximately neutral by adding dilute hydrochloric acid.

When the action is over, separate the mercury and run the liquid into hydrochloric acid (50 c.cs. strong acid : 50 c.cs. of water). The required product separates first as an oil and solidifies on cooling. Recrystallise from water. M.P. 47·°5.

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CHAPTER X.

AROMATIC ALCOHOLS, ALDEHYDS, KETONES, AND THEIR DERIVATIVES.

1. **Preparation of benzyl alcohol, $C_6H_5 . CH_2OH$, from benzyl chloride** (Meunier, *Bull. Soc. Ch.*, **38**, 159).—Boil 20 gms. of benzyl chloride under a reflux with 100 c.cs. of water and 15 gms. of potassium carbonate. When the smell of benzyl alcohol has gone (6-7 hours) extract with ether, dry with potassium carbonate, distil off the ether and collect the fraction 200°-210°.

Properties.—1. Colourless liquid, pleasant odour. B.P. 206·5°. Miscible with alcohol and ether. Has the properties of an aliphatic alcohol; it does not at all resemble phenol.

2. Warmed with strong hydrochloric acid benzyl chloride is formed slowly.

3. With strong nitric acid it is oxidised to benzaldehyd.

2. **Preparation of benzaldehyd, $C_6H_5 . CHO$.** (i) *From benzyl chloride.*—Heat together under a reflux 30 gms. of benzyl chloride with 40 gms. of copper nitrate in 250 c.cs. of water. (Several hours.)

Distil in steam till no more oily droplets pass over. Extract with ether and purify in the usual way, or convert to the bisulphite compound and decompose this as described under aldehyds, Part I. of this book. Yield, 18 gms. The copper nitrate acts as the necessary oxidising agent.

(ii) *From benzal chloride by direct hydrolysis.*—To 50 gms. of benzal chloride add 100 gms. of pptd. calcium carbonate and 250 c.cs. of water. Heat to 130° in an oil-bath (reflux). Distil in steam, shake the distillate with saturated sodium bisulphite, filter, wash the crystals with ether and distil in steam from concentrated sodium carbonate solution. Extract with ether, dry the extract with calcium chloride and distil off the ether.

Properties.—1. Colourless liquid. B.P. 179°. Characteristic smell of bitter almonds. S.G. 1·05.

2. A few drops exposed to the air on a watch-glass are soon oxidised to benzoic acid.

3. It gives the usual reactions of an aldehyd, except that it does not readily reduce Fehling's solution.

4. With ammonia it acts differently from fatty aldehyds, giving hydrobenzamide, $(C_6H_5CH)_3N_2$.

5. It forms oximes and hydrazones in the usual manner.

6. With aniline and all aromatic amino-bodies it condenses, forming bodies such as benzal aniline, $C_6H_5CH = NC_6H_5$. (Warm the mixture on a water-bath for an hour and filter. Recrystallise from alcohol.)

See also Malachite green, etc.

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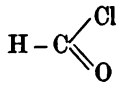
3. **Preparation of an aldehyd (tolyl aldehyd) by the Gattermann-Koch method** (*B.* **30**, 1622; **31**, 1149).—For full details see the papers quoted. The process consists of the passage of a mixture of pure dry carbon monoxide (2 vols.) and hydrochloric acid (1 vol.) through 30 gms. of freshly-distilled toluene containing 45 gms. of powdered aluminium chloride and 5 gms. of pure cuprous chloride. The whole is stirred mechanically in a wide-necked vessel. After several hours the viscous product is cooled, steam-distilled and the aldehyd purified by the bisulphite method. Yield, 20-23 gms. B.P. 204°. The active agent here appears to be formyl chloride



(unknown in free state) taking part in a Friedel-Craft reaction.

4. **Preparations involving reactions of benzaldehyd.**

(i) **Benzyl alcohol and benzoic acid by Cannizzaro's reaction** (R. Meyer, *B.* **14**, 2394).—Shake up 2 parts of benzaldehyd with 2 of caustic potash and 1 part of water till an emulsion is obtained. Set aside for several hours. Dissolve the solid product in water. Extract twice with ether. On acidifying the *aqueous* solution a ppt. of benzoic acid is obtained, and on drying the *ethereal* solution (K_2CO_3) and fractionating, benzyl alcohol is the product.

$$2C_6H_5 . CHO + KOH = C_6H_5 . CH_2OH + C_6H_5 . COOK.$$

(ii) **Benzoin,**

$$\begin{array}{l} C_6H_5 . CHOH \\ \quad\quad\quad\;\; | \\ C_6H_5 . C : O \end{array}$$

Mix 10 gms. of benzaldehyd, 20 c.cs. of absolute alcohol and 2 gms. of potassium cyanide in 8 c.cs. of water. Boil on a water-bath (reflux) for 30 minutes. Pour into a small beaker and cool. Filter the crystals and wash with alcohol.

Properties.—Small colourless prisms. M.P. 137.

(iii) **Benzil from benzoin.**—The crude benzoin is dried, powdered and heated with twice its weight of nitric acid, S.G. 1·4, for 2 hours on a water-bath. When the brown fumes disappear, pour into water, filter off the deposited crystals and recrystallise from alcohol.

$$C_6H_5 . CH(OH) . CO . C_6H_5 + O = H_2O + (C_6H_5CO)_2.$$

Properties.—1. Yellow prisms, M.P. 95°. Insoluble in water.

2. Boiled with alcoholic potash a violet colour is obtained.

3. Fused with potash, potassium benzilate results. From an aqueous solution of this, hydrochloric acid ppts. benzilic acid, $(C_6H_5)_2C . OH . COOH$.

(iv) **Oxime and hydrazone.**—(See Aliphatic aldehyds.)

(v) **Reaction with hydrocyanic acid. Mandelic nitrile and mandelic acid.**—To 40 c.cs. of saturated sodium bisulphite solution add 12 gms. of benzaldehyd. Stir till the addition product crystallises and filter on the pump. Wash with a little water, stir the crystals with a solution of 10 gms. of potassium cyanide in 20 c.cs. of water. Separate the oil which forms.

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$$C_6H_5CH.OH.SO_3Na + NaCN = C_6H_5CH.OH.CN + NaHSO_3.$$

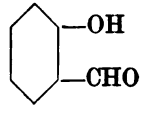
The nitrile is hydrolysed to mandelic acid by adding to 4 times its volume of strong hydrocloric acid and evaporating to crystallisation on a water-bath. Cool, extract with ether and allow the ether to evaporate. Recrystallise from benzene.

Properties.—Colourless crystals. M.P. 118°. It may be resolved into its optically active forms. (See p. 335 and Lewkowitsch, *B.* **16**, 1569, **17**, 2723.)

d-mandelic acid.—Prepare a culture medium of 0·5 gm. each of K_2HPO_4, NaCl and NH_4NO_3 in one litre of water; add a little of the acid, acidify with H_3PO_4 and sterilise in a cotton-wool-plugged flask. Infect with *penicillium glaucum*, and after a few weeks in a warm room, concentrate, acidify, extract with ether, evaporate and recrystallise from water. M.P. 133°. $[\alpha]_D^{20} = +156°·5$. (See pp. 483-8.)

l-mandelic acid.—The *d*-acid is destroyed by *Schizomycetes*.

5. **Preparation of Salicylal.**



Tiemann and Reimer's reaction (*B.* **9**, 423, 824, etc.).—Mix 100 gms. of caustic soda, 100 gms. of water and 30 gms. of phenol in a round-bottomed flask fitted with a reflux and a thermometer. Warm to 65° and gradually add chloroform (75 gms.), not allowing the temperature to rise above 70°. When all the chloroform has been added boil for 30 minutes, distil off the chloroform on a water-bath, dilute the residue with water, acidify with hydrochloric acid, and distil in steam. The *o*-body distils, the *p*-body remains behind as a solid. Extract the distillate with ether and separate as usual. The residue from this is treated with bisulphite and the additive compound washed with alcohol and warmed with dilute sulphuric acid. The liberated aldehyd is extracted with ether, dried over calcium chloride, and the ether distilled off. Yield, 20-25 gms. B.P. 196°.

$$C_6H_5OH + CHCl_3 + .H_2O = C_6H_4.(OH).CHO + 3HCl.$$

Properties.—1. Colourless oil. M.P. 20°; B.P. 196°; S.G. 1·17.

The residue from the first steam distillation is filtered whilst hot through a folded filter. The filtrate is cooled and extracted with ether. On evaporating the extract, yellow star-shaped crystals of the *p*-compound are obtained. Recrystallise from water. Yield, 2-3 gms. M.P. 115°.

6. **Preparation of acetophenone, benzophenone, etc.**—These may be made from benzene and the required acid chloride by Friedel and Craft's synthesis (see p. 355). Add the aluminium chloride to the benzene, cool with ice and add the acid chloride dropwise from a tap-funnel through the reflux. Stand for an hour after the reaction is over, then stir and pour into a beaker of ice and water. Extract the dark oil with benzene, separate, wash the extract with sodium carbonate, then with water. Dehydrate and distil off the benzene. Rectify the residue, collecting at 195°-200° for acetophenone, 290°-300° for benzophenone.

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CHAPTER XI.

PREPARATION OF AROMATIC ACIDS AND THEIR DERIVATIVES.

1. **Preparation of an acid by oxidation of a side-chain to carboxyl.**—(See Chapter IX.)

2. **Preparation of benzoic acid from benzo-trichloride.**

$$C_6H_5 . CCl_3 + 2H_2O = 3HCl + C_6H_5 . COOH.$$

Heat benzo-trichloride with some excess of milk of lime (reflux) till it goes into solution. Acidify with hydrochloric acid, filter and purify the pptd. benzoic acid as already described. (Illustrates the manufacturing process.)

3. **Preparation of an acid from a nitrile.**—The nitrile, obtained by Sandmeyer's reaction, is boiled (reflux) with moderately strong sulphuric acid (3 vols. acid : 2 vols. water). Purify by recrystallisation, extraction, etc., according to properties of acid. (Usually recrystallise from boiling water.)

4. **Preparation of an acid by Grignard's reagent.**—Treat the required reagent with carbon dioxide as fully explained in Part I., p. 352.

5. **Esterification.**—Best carried out with aromatic acids by Fischer and Speier's method, *q.v.* p. 320.

Alternatively, from the acid chloride. Benzoyl chloride and many other aromatic acid chlorides are remarkably stable to cold water, and esterification is readily carried out by mixing the alcohol with the acid chloride and carefully adding caustic soda till the smell of the chloride disappears. Separate the ester by the usual methods.

This is known as the **Schotten-Baumann reaction,** and it is very useful for identifying alcohols by preparing quickly a small quantity of the benzoic ester and finding its boiling-point. (See also preparation 8 below.)

6. **Preparation of acid chlorides.**—By the action of phosphorus pentachloride on the acid. 40 gms. of PCl_5 are placed in a 250 c.c. distilling flask, a reflux fitted and 22 gms. of benzoic or a corresponding amount of other acid added through the reflux.

Fractionate the product ($POCl_3$ boils at 100°).

Benzoyl chloride boils at 200°. It scarcely reacts with cold water, but benzoic acid is formed after heating for some time.

7. **Preparation of benzamide from benzoyl chloride.**—Grind in a mortar a few grams of benzoyl chloride with twice as much solid ammonium carbonate. Heat on a water-bath till the smell of benzoyl chloride disappears. Dilute

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with cold water, filter and recrystallise the product from hot water. M.P. 128°.

8. **Preparation of benzanilide, $C_6H_5 . CO . NH . C_6H_5$.**—Mix 5 gms. of benzoyl chloride and 6 gms. of aniline in a basin with sufficient caustic soda solution to maintain an alkaline reaction. The ppt. of benzanilide is quantitative. Filter and wash with (*a*) dilute hydrochloric acid, (*b*) water, and recrystallise from alcohol. M.P. 163°.

A similar reaction occurs with hydroxyl, $-NH_2$ and $=NH$ groups and affords a rapid preparation of benzoyl derivatives. (See preparation 5 above, and B. (1886) **19**, 3219.)

9. **Preparation of salicylic acid from phenol.** *Kolbe's reaction*, *J. pr. Ch.* 2) **10**, 95 ; **31**, 397.

$$C_6H_5ONa + CO_2 = C_6H_4\begin{cases} OH \\ CO_2Na \end{cases}$$

Perfectly dry sodium phenate is obtained by dissolving 12 gms. of pure caustic soda in 12 c.cs. of water and stirring in 28 gms. of phenol. The basin being clamped, evaporate *carefully* to dryness with vigorous stirring all the time. Grind up the product in a mortar and transfer to a 200 c.c. tubulated retort. A tube passes through the tubulus, guarded by a calcium chloride tube. Heat the retort in an oil-bath to 120° and draw dry air through by attaching the neck to an aspirator pump. Shake out the product whilst hot, powder it finely again and put it back in the retort. Pass in perfectly dry carbon dioxide at 110°, the delivery-tube being close to the phenate in the retort. In the course of 4 hours raise the temperature gradually to 190°, occasionally stirring up the mass with a glass-rod. Finally heat for an hour at 200° and allow to cool. Transfer the powder to a beaker (without disturbing the sublimate of phenol in the neck of the retort), wash out the retort with cold water and add to the contents of the beaker. Ppt. the free acid by rendering acid with strong hydrochloric. Filter the ppt. when cold, wash with cold water and recrystallise from hot water.

Properties.—1. White crystalline needles. Soluble in hot water and in alcohol. M.P. 159°.

2. Sublimes at 200° with decomposition.

3. Heated with soda-lime, phenol is produced.

4. Bromine water ppts. a tri-bromo derivative as with phenol.

5. Ferric chloride, even with very dilute solutions, gives a violet coloration discharged by sulphuric acid.

6. The acid and its methyl ester are excellent antiseptics.

7. The acid (or a salt) heated with a few drops of methyl alcohol and strong sulphuric acid gives the characteristic smell of methyl salicylate (oil of wintergreen).

10. **Preparation of salicylic acid (and *p*-oxy benzoic acid).**—When phenol is heated with carbon tetrachloride and caustic soda a reaction analogous to that of *Tiemann and Reimer* (p. 383) takes place. Heat together the reagents as there described ; distil off excess of tetrachloride, pass in carbon dioxide to decompose phenate and extract the phenol with ether. Ppt. the acids with strong hydrochloric acid. Filter and recrystallise from hot water.

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11. **Preparation of phthalimide from phthalic anhydride.**—Pass dry ammonia gas over heated phthalic anhydride in a boiling tube fitted with a cork carrying a long entrance and a short exit tube. Heating in an oil-bath, raise the temperature slowly from 130° to 230° during an hour. Crystallise from ether.

Properties.—1. White needles. M.P. 233°. (See also p. 328.)

2. It undergoes the Hofmann reaction with alkaline hypobromite, giving an amino acid. (See next preparation.)

12. **Preparation of anthranilic acid from phthalimide** (Hoogewerf and van Dorp, *Rec. trav. Ch.*, *P-B*, **8**, 173).—5 mols. of potash (in 10 % aqueous solution) and 1 mol. of bromine are mixed carefully (with cooling) and 1 mol. of phthalimide is added slowly. Cool and shake. Add 2 more mols. of 10 % potash and warm for 10 minutes. Acidify with acetic acid and add excess of copper acetate. The copper salt separates on standing. Suspend this, after filtering and washing, in hot water and decompose by saturating with hydrogen sulphide. Filter and crystallise the filtrate.

Properties.—1. Crystals, M.P. 145°. Soluble in water.

2. Employed in the synthesis of indigo.

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CHAPTER XII.

SOME IMPORTANT CONDENSATION REACTIONS.

1. **Cinnamic acid from benzaldehyd.** *Perkin's reaction.*—(See *J.C.S.*, 1868, 21, 53; 1877, 789, and the chapter on Perkin's reaction in *Spirit of Organic Chemistry*, Lachmann (Macmillan and Co.)).

$$C_6H_5CHO + CH_3CO_2Na \longrightarrow \left(\begin{matrix} C_6H_5CH.CH_2.CO_2Na \\ \cdot \\ OH \end{matrix}\right) \longrightarrow C_6H_5.CH:CH.CO_2Na$$

Acetic anhydride is used as the condensing agent.

Heat together 2 parts of benzaldehyd, 3 of acetic anhydride and 1 of powdered anhydrous sodium acetate, in a flask fitted with a long wide tube as reflux, and immersed in an oil-bath at 180°. After 8 hours pour whilst hot into a large flask containing excess of dilute sodium carbonate and distil off unchanged benzaldehyd in steam. Filter (boil with animal charcoal if necessary, and filter again) and add hydrochloric acid. Cinnamic acid is pptd. Recrystallise from hot water. Yield, 70 % of theory.

Colourless prisms. M.P. 133°.

Similarly, substituted benzaldehyds may be condensed with the sodium salt of any fatty acid with two hydrogen atoms in the primary group.

2. **Preparation of coumarin (*o*-hydroxy cinnamic lactone)** (Perkin, *A.* **147**, 203).—Make some *o*-hydroxy cinnamic acid by Perkin's reaction from salicylal and sodium acetate. On liberating the acid from its sodium salt the lactone forms spontaneously.

Properties.—Colourless crystals. M.P. 67°. Fragrant and aromatic odour (meadow-sweet).

3. **Preparation of a phthalein.** *Phenol phthalein.*

$$C_6H_4\left\langle\begin{matrix} CO \\ CO \end{matrix}\right\rangle O + 2C_6H_5OH = C_6H_4\left\langle\begin{matrix} C\left\langle\begin{matrix} C_6H_4OH \\ C_6H_4OH \end{matrix}\right. \\ O \\ CO \end{matrix}\right.$$

Heat 5 gms. of phthalic anhydride, 10 gms. of phenol and 4 gms. of strong sulphuric acid in a boiling tube in an oil-bath at 115°-120° for 8 hours. Pour the hot mass into cold water in a basin, boil off excess of phenol and filter from the insoluble powder. This is washed and dissolved in dilute caustic soda, filtered from insoluble matter and the filtrate acidified with acetic acid. On standing overnight phenol phthalein separates. Filter and dry.

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Purify by solution in alcohol and boiling with animal charcoal (very little). Filter hot, wash the residue with hot alcohol and evaporate filtrate and washings somewhat on a water-bath. Add 8 times the volume of cold water, filter quickly from the resinous matter which is thereby pptd., drive off the rest of the alcohol and set aside to crystallise. Yield, 2½ gms. Used as an indicator. (See also chapter on Dyes.)

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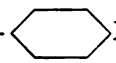
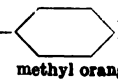
CHAPTER XIII.

PREPARATION OF DYES.

A. AZO DYES.

DIAZONIUM salts, in addition to the reactions already described, may be "coupled" with the *p*-position (usually) of phenols, amines, etc., giving rise to the so-called azo dyes.

E.g. $C_6H_4\langle^{SO_3Na}_{N_2OH}$ +  $N(CH_3)_2 = C_6H_4\langle^{SO_3Na}_{N:N-}$  $N(CH_3)_2$.

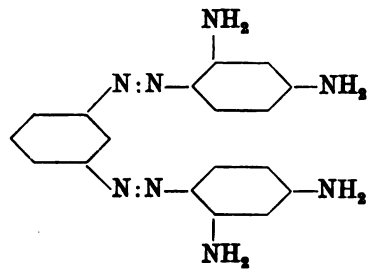
methyl orange.

Examples will now be described :

1. **p-Hydroxy-azo-benzene, $OH.C_6H_4.N:N.C_6H_4$.**—Add the solution of diazobenzene chloride to the theoretical quantity of phenol dissolved in caustic soda. Stand overnight and then salt out with common salt. Filter on the pump and wash. An orange dye is obtained.

2. **Helianthin (methyl orange, Orange III.)** [Reaction above].—Dissolve 10 gms. of sulphanilic acid in a solution of 2·1 gms. of anhydrous sodium carbonate in 100 c.cs. of water. Diazotise by adding (1) 4 gms. of sodium nitrite in 20 c.cs. of water, cooling to 0° and (2) 6 gms. of strong hydrochloric acid in 6 c.cs. of water. To this is added a solution made by dissolving 7 gms. of dimethyl aniline in 6 c.cs. of strong hydrochloric acid to 20 c.cs. of water. The whole, after thorough stirring, is rendered alkaline with caustic soda and salt added to assist pptn. of the dye stuff. Filter at the pump and recrystallise from hot water.

3. **Bismarck Brown.**



Prepared by dissolving *m*-phenylene diamine in hydrochloric acid and adding sufficient sodium nitrite to diazotise both the amino groups on one-third of

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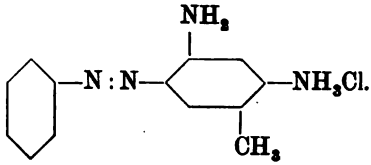
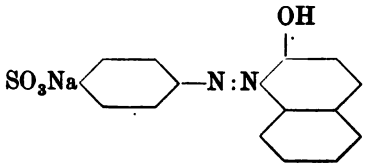
the weight of diamine taken. The dye stuff may be salted out with common salt.

4. **Chrysoidine.**



Diazotise aniline in hydrochloric acid solution and add the requisite quantity of *m*-toluylene diamine in hydrochloric acid solution. Salt out as before.

5. **Orange II.**



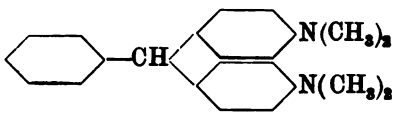
Dissolve 17·3 gms. of sulphanilic acid in the right amount of caustic soda. Cool with ice and dilute to 500 c.cs. Add 30 c.cs. of strong hydrochloric acid and diazotise as usual (7·2 gms. $NaNO_2$). The diazo salt will begin to separate. Now add gradually to a solution of β-naphthol in 4·5 gms. of caustic soda and 15 c.cs. of water, which has also been cooled and diluted to 150 c.cs. Stir thoroughly, stand an hour. Salt out and filter at the pump.

B. TRI-PHENYL METHANE SERIES.

1. **Preparation of tri-phenyl methane (the parent substance), $(C_6H_5)_3CH$,** by Friedel-Craft's reaction.—Mix 100 gms. of benzene and 20 gms. of chloroform. Stand overnight with calcium chloride. Filter into a flask, fit a reflux (wide tube) and add slowly 15 gms. of powdered aluminium chloride with constant shaking. Boil for half an hour. Cool and pour into cold water. Separate the upper layer of the methane solution in benzene, dehydrate with calcium chloride, distil off the benzene on a water-bath and then carry on with a free flame till 200° is reached. Now change the receiver and distil *in vacuo* till no more di-phenyl methane comes off and the process slackens. The receiver is again changed and the tri-phenyl methane distilled *in vacuo*. It comes over as an oil and crystallises in the receiver. Recrystallise from benzene and drive off the benzene of crystallisation at 100°. Yield, 14 gms. Colourless plates, M.P. 92°.

2. **Malachite Green** (*J.S.C.I.*, 1887, 433).

(*a*) *Preparation of the leuco-base.*



O. Fischer, *A.* **206**, 83, 122).—Mix 50 gms. of dimethyl aniline, 20 gms. of benzaldehyd and 20 gms. of fused zinc chloride. Heat for 4 hours in a porcelain basin on a water-bath, stirring frequently. The viscous mass is

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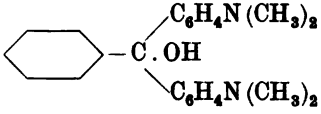
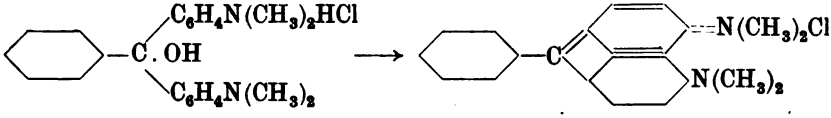
detached and transferred to a 500 c.c. flask by means of boiling water; unchanged reagents are distilled off in steam and the water in the flask poured away. The leuco base, which is a viscous mass sticking to the flask, is washed with water, dissolved in hot alcohol and filtered. Stand overnight and filter off the crystals, wash with alcohol and dry in air on filter-paper. Concentrate the liquor for a second crop.

(*b*) *Oxidation of leuco-base to colour-base.*



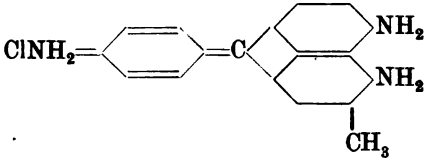
The leuco-base obtained above is dissolved in hydrochloric acid of 4N strength (10 parts of the base require 2·7 parts of anhydrous HCl). Dilute in a large flask with 800 parts of water and add gradually, with constant stirring, a thin paste of 7·5 parts of freshly-pptd. lead dioxide with water. After 5 minutes ppt. soluble lead by 10 parts of sodium sulphate in 50 of water. Filter off the lead sulphate and chloride. Treat the filtrate with 8 parts of zinc chloride in the minimum of water and then add saturated brine. Filter off the dye stuff, redissolve and salt out again. Dry in a basin on a water-bath. The actual dye stuff is derived from the colour-base by the elimination of water from the hydrochloride with formation of a quinonoid structure.



and the final product is the double salt with zinc chloride

$$3C_{23}H_{25}N_2Cl + 2ZnCl_2 + H_2O.$$

3. **Rosaniline (Magenta, Fuchsine).**



10 gms. of aniline, 40 gms. of commercial toluidine (36 % *p*, rest *o*) and 35 gms. of conc. hydrochloric acid are mixed in a 250 c.c. flask. 28 gms. of nitrobenzene are added (as oxidiser) and heated to 100° in an oil-bath. At this temperature add gradually 1·6 gms. of iron filings dissolved in hydrochloric acid. Fix an upright tube as reflux and heat to 180° for several hours till a portion of the melt taken out on a glass-rod solidifies completely when cold. Now fit an ordinary condenser, steam-distil any unchanged reagents and treat the remainder with 200 c.cs. of boiling water in a large beaker. Add hydrochloric acid till distinctly acid. Then add 12 gms. of salt, boil and pour off the solution from the insoluble residue. This last is broken up, powdered and extracted with much boiling water rendered acid with hydrochloric acid. Filter and set aside to cool. Filter again if necessary. Finally salt out, filter and recrystallise.

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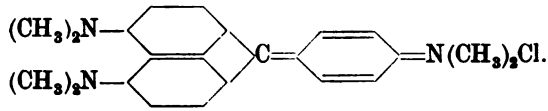
The colour-base (colourless) may be pptd. by adding ammonia to the magenta solution, whilst sulphur dioxide reduces it to the leuco-base (Schiff's reagent).

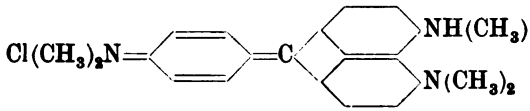
4. **Pararosaniline,** as above, using *p*-toluidine only.

5. **Crystal Violet.**



The formation can be illustrated by warming a mixture of a little Michler's ketone, dimethyl aniline and phosphorus oxychloride to 100°. When the colour changes to blue pour into water and a fine violet tint is obtained.

6. **Methyl violet B.** (*J.S.C.I.*, **1887**, 434).

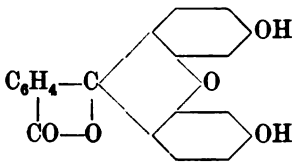


75 gms. of salt and 50 gms. of copper sulphate are powdered, well mixed and 40 gms. of phenol and 10 c.cs. of water are added and well stirred. Then add 100 gms. of dimethyl aniline and heat in a small flask on a water-bath for 8 hours to 55°. Pour into a basin containing 3 litres of water, containing milk of lime made from 40 gms. of quick-lime and 200 c.cs. of water. Decant the solution of salt and phenate, and extract with boiling dilute sulphuric acid. Filter from $CaSO_4$ and to the filtrate add pure sodium sulphate to ppt. the dye. Filter, wash, dissolve and salt out again from solution.

C. PHTHALEÏNS.

These may really be regarded as tri-phenyl methane derivatives. The preparation of one of them, phenolphthalein, has been dealt with. This is not a dye, however. The others are similarly prepared.

1. **Fluoresceïn.**



Mix intimately in a mortar 10 gms. of phthalic anhydride and 15 gms. of resorcinol. Transfer to a small glazed jar (an extract-of-meat pot answers excellently) and heat in an oil-bath to 180°. At this temperature add 4 gms. of powdered zinc chloride with thorough mixing and continue heating till the mass solidifies. Cool, chip out the melt with a cold chisel, grind in a mortar, boil with 150 c.cs. of water and 10 c.cs. of hydrochloric acid to remove basic zinc chloride. Filter, wash and dry the insoluble fluoresceïn. A red powder is obtained, soluble in alkalis.

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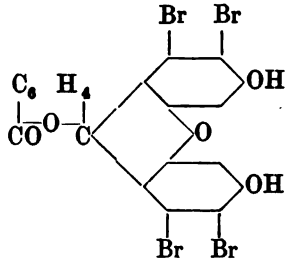
2. **Eosin** (Baeyer, *A.* **183**, 38).—By treating fluoresceïn with bromine, a tetrabromo body is formed (Eosin).



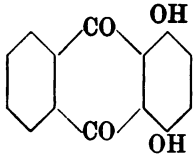
Place 15 parts of fluoresceïn in a flask, pour on to it 60 parts of 95 % alcohol and add 33 parts of bromine, drop by drop, from a separating funnel. Shake frequently. Stand for 2 hours, filter, wash ppt. with alcohol and dry it at 110° in an oven.

The ammonium or potassium salts are used for dyeing, as eosin itself is insoluble.

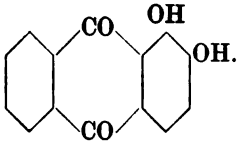
The ammonium salt is obtained by placing some ·880 ammonia in a dish, covering with stout blotting paper, and on it spreading out the eosin in a thin layer. The whole is covered with a bell-jar and left for some hours. The product should be completely soluble in water.

The sodium or potassium salt is made by mixing with the carbonate required, covering with water and heating on the water-bath. Boil the product with alcohol, filter and crystallise.

3. **Quinizarin,**



and Alizarin.



These bodies, derivatives of anthraquinone, can be obtained by condensations with phthalic anhydride, using, for quinizarin, hydroquinone (5 parts), phthalic anhydride (20 parts) and strong sulphuric acid (100 parts to 10 of water) at 170° for 3 hours and then at 200° for 1 hour.

Alizarin similarly, using pyrocatechol.

These methods are now of historical and theoretical interest only. The following methods illustrate large-scale processes.

(*a*) **Quinizarin** (English patent, 973 of 1894).—A mixture of 10 parts of anthraquinone, 10 of crystallised boric acid and 200 of strong sulphuric acid is heated in a flask. At 260°-280° an energetic reaction commences. When the evolution of sulphur dioxide has ceased, the reaction is complete. (Avoid heating too long or purpurin will be formed.)

Pour the cooled product into water, filter off the quinizarin and purify by solution in alkali and repptn. with acid.

(*b*) **Alizarin from sodium β-anthraquinone monosulphonate.** (i) *Anthraquinone from anthracene.*—20 gms. of anthracene are mixed with 200 c.cs. of

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glacial acetic acid and boiled in a flask fitted with a reflux. During an hour add gradually a solution of 40 gms. of chromic acid in 150 gms. of glacial acetic acid and 20 of water. Cool, pour into much water, leave for an hour and filter off the anthraquinone. Wash with dilute sulphuric acid and then with water. Dry and purify by sublimation. Yield, 20 gms.

Yellow needles, M.P. 285°.

Note.—On the large scale the oxidation is done in aqueous solution, but requires about 16 hours at 95°.

(ii) *Preparation of sodium β-anthraquinone monosulphonate.*—Sulphonate powdered anthraquinone with an equal weight of fuming sulphuric acid of S.G. 2 (50 % anhydride) in a round-bottomed flask, heated to 160° in an oil-bath during 1 hour. Allow the product to flow very slowly (care !) into much boiling water, filter from unchanged anthraquinone, neutralise the filtrate with soda and cool. Most of the salt separates in silvery leaflets, but concentration of the liquor gives a further yield.

(iii) *Oxidation of the sulphonate to alizarin* (Perkin, *J.S.C.I.*, **1883**, 213).—A mixture of 10 parts of the sulphonate, 30 of caustic soda, 2 of potassium chlorate and 40 of water is heated in an autoclave for 20 hours to 170°. Cool, extract the melt several times with boiling water, and then acidify the extract with strong hydrochloric acid whilst boiling. Cool, filter off the alizarin, wash, press and dry at 120°.

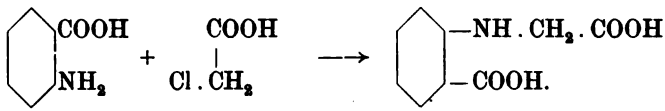
Properties.—1. Yellow powder, M.P. 289°. Readily soluble in alcohol. Sublimes.

2. Readily soluble in alkalis to a deep red solution.

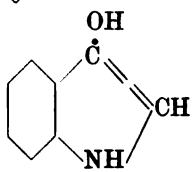
D. INDIGO.

Heumann's synthesis of indigo. (*B.* 1890, **23**, 3432.)

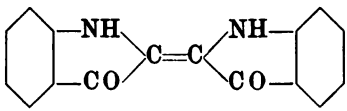
Reactions.



Fusion with potash converts this to indoxyl,



which on oxidation ⟶ indigo



(i) *Preparation of phenyl glycine o-carboxylic acid.*—33·6 gms. of anthranilic acid * and 9·4 gms. of chloracetic acid are dissolved in 100 c.cs. of water and 11·2 gms. of potash. Heat under a reflux on a water-bath to 60°-80° for 2

* For synthesis of this, see p. 386.

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hours. Neutralise with hydrochloric acid and set aside. Filter off the acid, and recrystallise from hot water; work up the mother-liquor for a second crop. M.P. 200°.

(ii) *Indoxyl and indigo.*—1 part of this acid and 3 parts of potash are fused in a metal basin with stirring. Regulate temperature carefully between 180° and 200°. When the colour no longer deepens pour the melt into 200 c.cs. of water. Oxidise by drawing a rapid current of air through the liquid, in a flask, by means of a filter-pump. When no more indigo separates from a filtered test portion on similar treatment, filter, wash with water, hydrochloric acid, alcohol and dry.

Properties.—1. Dark blue powder, coppery lustre. Insoluble in water.

2. May be recrystallised from aniline or paraffin, or sublimed.

3. Soluble in warm strong sulphuric acid (sulphonic acid).

The parent substance of the indigo group is

Indol (Benzopyrrol) $C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle CH.$

Properties.—1. White crystalline substance. M.P. 50°. Not very soluble in cold water, but readily in hot water, alcohol and ether. Possesses a characteristic odour and is volatile in steam.

2. It gives a violet-blue colour with sodium nitroprusside, changing to blue on adding acetic acid.

3. Pine-shaving test.—Moisten a pine shaving with conc. HCl and place it in a test-tube at the bottom of which is a small quantity of alcoholic indol solution. Shake to moisten the shaving, take out the latter and stand for a few minutes or dry on a water-bath. A bright red colour appears on the shaving. This test is characteristic of pyrrol (C_4H_5N, liquid of B.P. 133°) and many indol derivatives.

Skatol has similar properties. It is β-methyl indol, the same hydrogen atom being replaced as in indoxyl. (M.P. 120°, p. 394.)

Indican (urinary). See p. 299. Do not confuse with the glucoside (p. 326).

Tryptophane (Indol α-amino-propionic acid), $C_{11}H_{12}N_2O_2$. This is an important decomposition and hydrolysis product of proteids (Emil Fischer, Hopkins and Cole).

Properties.—1. White crystalline solid. M.P. 252°, but decomposing above this to indol and skatol, etc.

2. Gives a purple colour in the pine-shaving test in alcoholic or aqueous solution.

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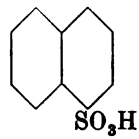
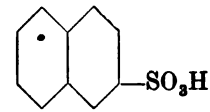
CHAPTER XIV.

NAPHTHALENE DERIVATIVES.

1. **Preparation of the mono-sulphonic acids.**

(α) 

(β) 

Heat 60 gms. of sulphuric acid on a water-bath in a long-necked flask. Gradually add 50 gms. of powdered naphthalene, a few grams at a time. If the β acid is required, the temperature is now raised to 160° (oil-bath) for several hours. If the α acid is required continue for 6 hours at 80° on the water-bath. Dissolve the crude product in 1500 c.cs. of water, filter from unchanged naphthalene, heat to boiling and neutralise with a slight excess of the carbonate of lead, barium or calcium. Filter the boiling liquid, first through a cloth and then through a filter (hot-water funnel). On cooling, the β-salt crystallises. Evaporate to half bulk for a second crop; evaporate the liquor from this till it is semi-solid; this is chiefly the β-salt. To purify the α from the β, boil with 85 % alcohol in which the α is readily soluble.

In the cold, the α salt (Pb) dissolves in 27 parts of water or 11 of alcohol.
" " " β " " " " 115 " " " 305 "

The sodium salt is prepared by suspending the lead, etc., salt in boiling water and adding the right amount of sodium carbonate. Filter and crystallise.

The free acid is obtained as for benzene sulphonic acid (*q.v.* p. 356).

2. **Preparation of α and β naphthols.**—Fuse 45 gms. of caustic soda and 2 c.cs. of water in an iron or nickel basin. Stir with a thermometer protected by a small glass-tube over the bulb. (Care of eyes and hands!) At 280° add 15 gms. of the sodium sulphonate, sprinkling it in slowly and keeping the temperature at 280°. Raise to 300°, and when frothing ceases, to 310°. When the mass separates into two layers and darkens, pour out on to a clean tile. When cold dissolve in water. Acidify with hydrochloric acid (1 : 1) and filter off the pptd. naphthol. Recrystallise from boiling water.

Properties.—1. α-naphthol: M.P. 95°; B.P. 282°. β-naphthol: M.P. 122°; B.P. 288°.

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2. With ferric chloride α-naphthol gives a flocculent violet ppt., β-naphthol a green coloration and a ppt. of β-di-naphthol.

3. **Preparation of α-nitro-naphthalene** (Witt, *Chem. Ind.*, **1887**, 216).—Mix 8 parts of conc. nitric acid (S.G. 1·4) with 10 parts of conc. sulphuric acid. Place in a round-bottomed 500 c.c. flask and sprinkle in slowly, with constant shaking, 10 parts of finely-powdered naphthalene. Do not allow the temperature to rise above 50° until the end, when it is raised to 60°, and the mass poured into cold water. The nitro-naphthalene sinks and is separated, washed, and any naphthalene present is steam-distilled off. The residue is again separated and allowed to solidify. M.P. 61°; B.P. 304°; S.G. 1·33.

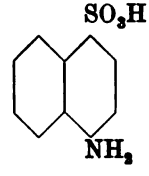
It is used for making α-naphthylamine.

4. **Preparation of α-naphthylamine** (Witt, *Chem. Ind.*, **1887**, 215).—80 gms. of fine iron filings, 4 gms. of strong hydrochloric acid, and 40 c.cs. of water are placed in a round-bottomed flask and heated to 50°. 60 gms. of α-nitro-naphthalene are added a little at a time with constant stirring. The temperature is kept at 70°-80°. When all is added, shake and continue till there is no further rise of temperature. Now heat to 90° until a test portion will dissolve clearly in hydrochloric acid (no nitro-naphthalene left). Now make alkaline by milk of lime, cool and filter on the pump. Dry on the pump as far as possible, transfer to a small retort connected air-tight to a distillation flask as receiver and distil *in vacuo* with a small flame. First water comes over, then the amine. Dry the solidified mass by filter-paper and redistil.

Properties.—1. M.P. 48°; B.P. 300°. Almost insoluble in water. Soluble in dilute hydrochloric acid.

β-naphthylamine is prepared from β-naphthol by treatment with zinc chloride dissolved in ammonia. (B. 1880, **13**, 1300.)

5. **Preparation of naphthionic acid.**



(Neville and Winther, *J.C.S.* (**37**) 632).—Heat 1 part of α-naphthylamine with 5 parts of strong sulphuric acid to 180° (and no higher!) on an oil-bath, till a test portion dissolves completely in alkali. Pour into water, neutralise with caustic soda and salt out the sodium salt. Filter, dry at 100° and extract with alcohol to remove any naphthylamine. It is employed in the manufacture of various dyes, notably Congo-red. This is illustrated below.

To make phenyl-azo-naphthionic acid (Congo red), dissolve 2·5 parts of naphthionic acid in strong sodium acetate solution. Cool, and add diazo-benzidene chloride (from 0·9 parts of benzidene, 2·5 of hydrochloric acid, 50 of water, and 0·65 of sodium nitrite in 15 of water).

The sodium salt is red, the free acid blue.

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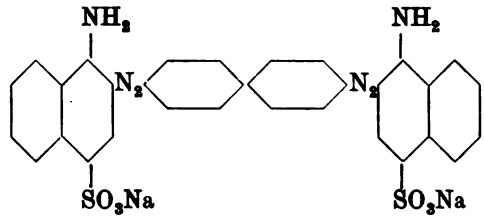

FORMULA OF CONGO RED.

Fast red A is made by coupling diazotised naphthionic acid with β-naphthol.

6. **Preparation of naphthoquinone.**—As for anthraquinone, p. 393.

1. Naphthoquinone sublimes in the form of yellow needles. It dissolves with difficulty in alcohol and ether, giving golden yellow solutions which exhibit a beautiful green fluorescence when dilute.

2. Its solution reduces ammoniacal silver oxide on boiling.

3. Boiled with nitric acid in the presence of silver, it is oxidised to silver phthalate, which is deposited on cooling in the form of rhombic crystals.

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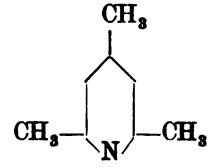
CHAPTER XV.

SOME HETERO-CYCLIC BODIES.

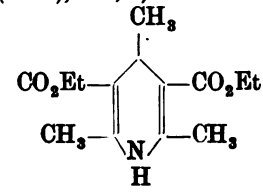
A. PYRIDINE GROUP.

PYRIDINE itself (B.P. 116°) is not easily synthesised, but an important derivative readily prepared is collidine, 1, 3, 5 tri-methyl pyridine,



1. **Preparation of collidine** (Hantzsch, *A.* (1882), **215**, 1).

(i) *Dihydro-collidine-dicarboxylic ester.*



A mixture of 25 gms. of aceto-acetic ester and 8 gms. of freshly made aldehyd ammonia are heated to 100°-110° in a small beaker, for 3 minutes, stirring with a thermometer. Then treat the warm mixture with about an equal volume of dilute hydrochloric acid, S.G. 1·05. Stir till it solidifies. Powder, put on a filter (pump), wash with dilute hydrochloric acid and dry at 100°. Purify if required by recrystallisation from alcohol.

Properties.—M.P. 131°. Colourless tablets with bluish fluorescence.

(ii) *Oxidation of above to collidine-dicarboxylic ester.*—The crude ester obtained in (1) is treated with an equal volume of alcohol in a small flask. It partly dissolves. Lead in nitrous fumes (from arsenious oxide lumps and strong nitric acid) which have been passed through an empty wash-bottle. Cool the flask with water, and continue till all the ester has gone into solution. Evaporate the alcohol on a water-bath, render alkaline with sodium carbonate solution and extract the separated oil with ether. Dry the extract with a little solid potash, evaporate the ether and distil the residue.

Properties.—Yellow oil. Boils at 290°-310° for following preparations.

(iii) *Potassium collidine dicarboxylate.*—Hydrolyse the crude ester obtained in (ii) by boiling 1 part of the ester with 2 of potash and 3 of alcohol for

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5 hours on a water-bath (reflux). Cool, pour off the alcoholic liquor, filter, and wash the product with alcohol, ether and then dry.

(iv) *Collidine by lime distillation.*—Mix the dry potassium salt from (iii) with twice its weight of slaked lime. Place in the closed end of a combustion tube 50 cms. long. Make a passage above the contents by gently tapping the tube in a horizontal position, and then put in a wad of asbestos to keep the contents in place.

Heat in a furnace tilted so that the tube inclines downward slightly, the tube being connected by an adapter to a receiver. Start the heating at the closed end, gradually turning on the burners till the whole is heated strongly.

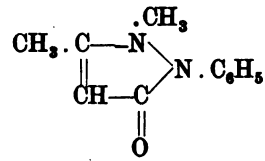
Extract the distillate with ether, dry with potash, distil off the ether and rectify.

Properties.—1. Yellow green liquid with disagreeable odour. B.P. 172°.

2. It has the properties of a tertiary base.

B. PYRAZOLE GROUP.

2. **Preparation of anti-pyrine,** 1-phenyl-2, 3-di-methyl pyrazolone. (Knorr, *A.* **238**, 137.)



In the cold mix aceto-acetic ester with phenyl hydrazine in molecular proportions. Heat to 100° (reflux). Alcohol is eliminated and phenyl-methyl-pyrazolone is formed. Add enough alcohol to dissolve it, add 1 molecular proportion of methyl iodide and digest again on the water-bath. Decolorise by passing in sulphur dioxide, distil off the alcohol and separate the base (a heavy oil) by making alkaline with strong caustic soda. Recrystallise from toluene.

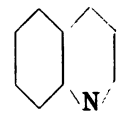
Properties.—1. Colourless crystals. M.P. 113°. Readily soluble in water or alcohol.

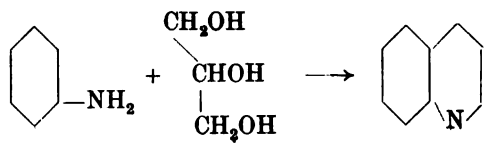
2. Strong basic properties (monacid).

3. Aqueous solution gives a red colour with ferric chloride, blue-green with nitrous acid.

4. It is a valuable febrifuge.

C. QUINOLINE GROUP.

3. **Preparation of quinoline.**  (Skraup's synthesis).

Reactions. 

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In a 1½ litre flask mix 38 gms. of aniline, 24 of nitro-benzene and 120 of glycerol. Add with stirring 100 gms. of sulphuric acid, attach a long air-cooled reflux and heat on a gauze till a reaction sets in (10-15 minutes). Remove the flame and allow the reaction to finish. Now boil gently for 2-3 hours on a sand-bath. Dilute the dark product, after cooling, with water. Remove nitro-benzene by steam-distilling and make the residue alkaline with strong caustic soda solution. Distil off the quinoline (and aniline) in steam. Treat the whole of the distillate with dilute sulphuric acid till the two layers disappear and excess of acid is present. Cool well, add sodium nitrite till starch iodide paper turns blue with a test-drop and boil on a water-bath. The aniline is thus changed to phenol. Now make alkaline again and steam-distil. Extract the distillate with ether, evaporate off the ether from the extract and distil the residue at 237°. Yield, 40 gms.

Properties.—1. Pale yellow oil. Insoluble in water, soluble in organic solvents.

2. Acts as a tertiary base, giving chlor-platinate, and a quaternary salt with alkyl iodides.

3. A solution of bromine in chloroform gives a ppt. of the dibromide.

D. PURINE GROUP.

Properties of uric acid, $C_5H_4N_4O_3$, the chief member.

1. White crystalline solid, charring with decomposition on heating; nearly insoluble in water, insoluble in organic solvents. The alkali salts are slightly soluble in warm water, especially that of lithium. Hence the acid dissolves on boiling with alkaline hydroxides or carbonates though not readily.

2. Reduces Fehling's solution on boiling (use the sodium salt).

3. Gives the murexide test (see p. 407).

For *Alkaloids*, see p. 408.

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BOOK V.

ORGANIC ANALYSIS.

PART I.

QUALITATIVE ORGANIC ANALYSIS.

In organic qualitative analysis, it is impossible to give a definite systematic scheme such as we have in inorganic chemistry. This is partly owing to the enormously varied nature of organic bodies, and partly to the fact that we are not dealing with reactions between ions. The student therefore will be thrown on his own resources and knowledge. The wider his experience of different compounds, the easier he will find it to identify and separate mixtures of organic substances.

We may place the reactions on a systematic basis to some extent as follows:

General Tests.

I. Heat in an ignition tube and on a piece of porcelain or platinum foil, noting all odours evolved, colour changes, gases, and the nature of residues.

II. Detection of the elements, C, H, O, N, S, P, halogens, metals.

III. Treat with water and both red and blue litmus.

IV. Action of caustic soda solution (*a*) cold, (*b*) hot.

V. Heat with soda-lime.

VI. Treat with mineral acids (dilute hydrochloric; strong sulphuric).

VII. Treat with bromine water; also with alkaline permanganate (von Baeyer's reagent).

VIII. Treat with ferric chloride solution.

IX. Treat with sodium bisulphite, Fehling's solution and ammoniacal silver oxide.

X. Determine melting and boiling points, and specific gravity.

XI. Apply special tests and confirmatory experiments.

It should be understood that these reagents will frequently give negative tests, and that a given reagent does not always act in the same manner. Usually, however, by the time the first nine tests have been applied, a good idea will have been obtained as to the class of substance to which the body belongs.

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The above tests are carried out as follows and lead to the general results indicated.

Test I.—Heat about half a gram in an ignition tube, and another small portion on porcelain or platinum foil, with full access to the air.

(i) The substance melts, boils and distils unchanged. Little information is given here. The smell of the vapour may be some guide.

(ii) A residue on the porcelain or foil is almost certainly a metallic carbonate (Na or K), oxide or metal (Ag, Pt).

(iii) Substance melts and chars. Usually water and various vapours are evolved.

(*a*) Smell of burnt sugar. Carbohydrates. Tartrates.
(*b*) Smell of burnt cotton. Cellulose. Citrates.
(*c*) Smell of burnt wool. Some nitrogenous bodies, *e.g.* alkaloids.
(*d*) Smell of ammonia. Various nitrogen compounds, especially urea, guanidine.

Test II.—The tests for the elements are carried out as follows :

Carbon and hydrogen.—Mix intimately with copper oxide and heat in an ignition tube. Carbon dioxide and water are evolved.

Halogens.—Thoroughly oxidise a piece of copper gauze. Place on it a small piece of the substance and heat in the flame. A fine blue-green flame indicates a halogen. To see which, mix intimately with pure quick-lime and heat very strongly in a small, hard glass test-tube. Cool, extract with dilute nitric acid and test the filtered solution with silver nitrate.

Sulphur, phosphorus, nitrogen.—Heat the substance in a small, hard glass ignition-tube with a *small* piece of freshly-cut sodium ; gently at first, finally as strongly as possible.

Phosphorus	forms	sodium	phosphide.
Sulphur	,,	,,	sulphide.
Nitrogen	,,	,,	cyanide.

Dip the hot tube into a few c.cs. of cold water in a basin (care ! unchanged sodium).

A smell of PH_3 is observed. Phosphorus.

Dip a silver coin into the solution. A black stain ; sulphur. Filter the solution and add 1 c.c. of caustic soda and 1 c.c. of freshly-made ferrous sulphate solution and boil.

$$6NaCN + Fe(OH)_2 = Na_4Fe(CN)_6 + 2NaOH.$$

Add 1 drop of ferric chloride solution and dissolve the ppt. by adding excess of dilute hydrochloric acid. A ppt. of prussian blue, or a blue (or green) coloration = nitrogen.

Note.—The presence of sulphur *may* interfere with this test, as NaCNS is formed. This gives a red colour with ferric chloride, so that both nitrogen and sulphur are detected at once. The formation of thio-cyanate is by no means certain, however ; it is best to use an excess of sodium in any case.

The same solution as above will, if sulphur be present, give a fine purple coloration with dilute sodium nitroprusside solution ; it may also give a smell of H_2S if warmed with dilute hydrochloric acid. (Try lead acetate paper.)

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Castellana (*Gaz. Chim. It.* 1904, **34** (2) 359) recommends a mixture of 2 parts of potassium carbonate and 1 of magnesium powder, instead of sodium.

Oxygen.—There is no test for oxygen. The only way to prove its presence (apart from decomposition products, readily recognised groupings containing it, etc.) is to make a complete quantitative analysis of the other elements found. If the percentages do not add up to 100, then the difference will be oxygen. This, however, will not be necessary in ordinary work in identifying *known* substances. It may be necessary in the analysis of a newly discovered body.

After having noted the general appearance of the body and carried out tests I. and II., a fair idea of the nature of the body should have been obtained. The results of test II. may be summarised by dividing bodies into the following classes, according to their composition.

1. Bodies containing C and H (and O) only.
2. „ „ C, H and N . (O) only (sometimes halogen also).
3. „ „ C, H, and halogens.
4. „ „ C, H, and S.
5. „ „ C, H, N, S.
6. „ „ P, As, etc., are rarely met with.

Note.—Coloured bodies may be:

Quinones, diketones, nitro-bodies, aniline (due to impurity), azo bodies, nitroso-compounds, dyes, etc., etc.

Confirmatory tests and physical constants have been fully discussed under the preparation of each substance.

Class I.—Containing C, H, (O) only.

Test III.—Shake the substance with water. Warm if nothing happens. Test with both blue and red litmus.

(i) *Soluble in cold water.*

(*a*) Acid reaction. The lower acids as formic, acetic, etc., oxalic, tartaric, etc.; oxy-acids as lactic.

(*b*) Neutral reaction. Alcohols, a few esters, polyhydric phenols, aldehyds, ketones, sugars.

(ii) *Soluble in hot water, not very soluble in cold.*—Some aromatic acids, monohydric phenols, starch.

(iii) *Insoluble in water, or only slightly dissolved.*—Higher acids, phenols, most esters, hydrocarbons (acid chlorides and anhydrides gradually react). Ethers.

Test IV.—To the substance add cold, fairly strong caustic soda solution. Warm. Afterwards render acid with hydrochloric.

(i) *The substance dissolves in the cold.*—Acids, phenols, pseudo-acids. Hydrochloric acid reppts. aromatic acids, phenols, etc.

A phenol and an acid may be distinguished by treatment with sodium carbonate. The acid only causes evolution of CO_2.

A carboxylic acid should be heated with soda-lime, and the resulting hydrocarbon (or derivative) may be recognised.

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(ii) The substance is acted upon slowly, dissolving on warming, with or without decomposition.

(*a*) *Originally had a faintly acid reaction.* Lactones, esters, anhydrides.

(*b*) *Neutral reaction.* Some sugars and most aldehyds turn brown.

(iii) *No action.*—Esters, hydrocarbons, higher alcohols.

Test VI.—Add dilute HCl to the substance and boil for some time. Cool.

(i) Salts of aromatic acids give a ppt. of the corresponding acid.

(ii) Silver and lead salts give a ppt. of the chloride.

(iii) Esters and acid derivatives will be decomposed gradually. Note whether the smell of acetic or benzoic acid becomes noticeable.

(Acetyl or benzoyl derivatives.)

If solid, heat with strong sulphuric acid.

(i) If no charring takes place and (*a*) CO alone evolved: Formic acid and salts, ferrocyanides, lactic acid and salts.

" " " " " (*b*) $CO + CO_2$ are evolved: Oxalic acid and salts.

" " " " " (*c*) Pungent vapours of acids: Acetate, butyrate, some aromatic acids, phenols, some esters.

In case of acid smell, add a drop of alcohol and warm again. Some characteristic ester may be noted.

(ii) Slow charring and evolution of CO and CO_2. Citric acid and salts.

(iii) Rapid charring.

(*a*) Evolution of CO and CO_2. Tartrates.

(*b*) Ditto, with smell of burnt sugar, pungent vapours, SO_2, etc. Carbohydrates.

(*c*) No gases evolved. Polyhydric phenols and derivatives.

Test VII.—Bromine water is decolorised in the cold by all unsaturated bodies, without evolution of HBr. Baeyer's reagent is also decolorised (ppt. of MnO_2) by unsaturated bodies, also by formic acid, aldehyds, and aliphatic oxy acids.

Test VIII.—Add ferric chloride solution to the neutral solution of the body.

(*a*) Reddish coloration; ppt. on boiling (basic salt). Formic and acetic acids and salts.

(*b*) Intense colours (greens, violets, purples) from all phenolic derivatives.

(*c*) Deep yellow colour. Lactic, citric, tartaric acids.

Test IX.—Aldehyds and ketones all give crystalline ppts. with sodium bisulphite (saturated solution).

Aldehyds reduce Fehling's solution and give a silver mirror when boiled with ammoniacal silver oxide. Ketones do not.

Test X.—If the class of body has been discovered, its melting or boiling point should be found. This serves to distinguish the members of a class.

In the case of sugars, whose melting points are not reliable, the osazone should be made and its melting point found.

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Class II.—Containing C, H, N, (O).

Particularly noticeable either by smell or appearance are:

Acetamide, amines, nitrobenzene, aniline and dimethylaniline, nitro-phenols, azo-bodies, pyridine, indol.

Test III.—Water and litmus. (i) *Soluble in cold water.*

(*a*) *Acid.*—Nitro-phenols. Salts of weak bases as aniline.

(*b*) *Alkaline.*—Aliphatic amines. Aromatic diamines.

(*c*) *Neutral.*—Salts of aliphatic amines. Some amino-acids and phenols.

(ii) *Soluble in hot water.*—Some amides. Some purine derivatives. Nitraniline, acetanilide.

(iii) *Insoluble or very sparingly soluble.*—Uric acid group, nitric esters, nitro-derivatives, aniline and aromatic amines, alkaloids, proteids, nitriles, and iso-cyanides, higher amides and oximes, hydrazones, urethanes, benzanilide, etc.

Test IV.—Caustic alkali test. (i) *Bodies insoluble in water dissolving readily in cold caustic soda.*—Nitro-acids and nitro-phenols (generally with intense coloration). Some oximes, uric acid, etc.

(ii) *Bodies evolving ammonia (or amines) on warming.*—Ammonium salts, amides, aldehyd-ammonias, salts of aliphatic amines.

(iii) *Bodies evolving ammonia gradually on prolonged boiling.*—Amides, nitriles, imides, urethanes, nitramines, derivatives of soluble aliphatic amines.

(iv) *Bodies from which an insoluble base separates.*

(*a*) *In the cold.*—Salts of aromatic amines, etc.

(*b*) *On boiling.*—Acetyl, benzoyl, etc., derivatives of insoluble amines, *e.g.* acetanilide.

Test VI.—(i) Dilute HCl, cold, then hot.

(*a*) *The body dissolves.*—All basic bodies, as amines, hydrazines, alkaloids. Hydrochlorides are formed.

(*b*) *The body hydrolyses.*—Most oximes and hydrazones, higher amides, acylamino acids (*e.g.* hippuric), in which case the aromatic acyl group if present will be pptd. on continued boiling.

(ii) **Strong H_2SO_4.**—Not very conclusive results in this class. Bases form sulphates, and some bodies undergo sulphonation.

Test VII.—Bromine water.—Unsaturated bodies decolorise it; diazo-bodies, amines and some azo-bodies give ppts.

Test IX.—Ammoniacal silver oxide. Fehling's solution.

(*a*) Positive results indicate reducing agents, *e.g.* substituted hydrazines.

(*b*) Boil the body with hydrochloric acid, neutralise and test again. Positive results indicate hydrazones, oximes, semi-carbazones, osazones, which yield reducing agents on hydrolysis.

Test XI.—Of special importance is the biuret test.—Heat the substance carefully till water is evolved and the mass tends to solidify. Cool and add a few drops of water, a drop of copper sulphate and some caustic soda solution. A violet or pinkish coloration.

Urea.—Proteïns as a class.

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Murexide test.—Evaporate a little of the body with a few c.cs. of strong nitric acid (water-bath). An orange or red residue remains which turns to a fine purple with ammonia. Uric acid, alloxan and all the purine derivatives.

Class III.—Bodies containing C, H, (O). Halogens.

Find which halogen is present.

The following have characteristic smells:

Chloroform, iodoform, chloral and chloral hydrate, chloracetic acid.

Test III.—Water and litmus. (i) *Soluble in cold water. Acid reaction.*—Aliphatic halogen-substituted acids and aldehyds. *Neutral reaction.*—Halogen-substituted alcohols.

(ii) *Soluble in hot water. Acid reaction.*—Aromatic halogen acids. Substituted phenols. (Differentiate with sodium bicarbonate.)

(iii) *Insoluble in water.*—Halogen-substituted hydrocarbons, esters of halogen-substituted acids, substituted ketones, ethers, etc.

(iv) *React with water and evolve hydrochloric acid.*—Acid chlorides (some very slowly).

Test IV.—Caustic soda; cold, then hot.

(*a*) If the body is soluble in water, similar results to those of Class I. are obtained.

(*b*) If the body is insoluble in water it is better to use alcoholic alkali and a reflux.

Halogen-substituted hydrocarbons, NaCl, etc., pptd. at once, and an unsaturated hydrocarbon is evolved.

Very slow, or no action. Saturated aromatic halogen compounds. In any case, boil with alcoholic silver nitrate. Aliphatic iodine derivatives and acid halides rapidly cause a ppt. of silver halide.

Substituted esters, acids, ketones, α-halo-aromatic acids, chlorine- and bromine-substituted side-chain bodies produce a ppt. slowly.

In general, the class of body to which the compound belongs may be found as in Class I.

Class IV.—Bodies containing C, H, S.

These bodies are limited in number. We may expect:

Sulphonic acids and salts; sulphites, sulphates, sulphides; mercaptans, sulphuric acids, sulphoxides, sulphones; sulphonal; thiourea and allied bodies; thio-carboxylic acids, esters and salts; thiophenates (sulphocarbolates).

Test III.—Water and litmus. (*a*) *Soluble.*

(i) *Acid reaction.*—Soluble sulphonic acids; some thio-carboxylic acids.

(ii) *Neutral reaction.*—Salts of the above acids. Aliphatic sulphoxides.

(iii) *Alkaline reaction.*—Sulphine base.

(*b*) *Insoluble.*—Alkyl sulphates and sulphites (decompose very readily), mercaptans, sulphides.

Test IV.—Caustic soda.

(i) *Readily soluble.*—Acids as above. Mercaptans.

(ii) *Hydrolysis occurs.*—Alkyl sulphites and sulphates; thio-substituted esters.

Heated with solid soda-lime, sulphonic acids give phenols or alcohols.

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Test XI. Special tests.—There is nothing here of great importance. Note, however, that should **halogen** be present in addition to the elements already noted in this group, we are probably dealing with sulphonchlorides, of which the chloride of benzene sulphonic acid is most commonly met with.

Class V. Bodies containing C, H, (O), N, S.

This class comprises :

Thio-urea ; thio- and isothio-cyanates (smell like mustard oil) ; nitro- and amino-sulphonic acids (*e.g.* sulphanilic acid) ; sulphonamides and sulphonimides (*e.g.* saccharin, $C_6H_4\begin{matrix}SO_2\\CO\end{matrix}\!\!>\!NH$).

Test III. Water and litmus.

(*a*) *Soluble in cold water.*—Thio-urea. Thio-cyanic acid salts. Some nitro-sulphonic acids. Saccharin (very sweet).

(*b*) *Soluble in warm water.*—Amino-sulphonic acids. Lower sulphonamides.

(*c*) *Insoluble.*—Thio-cyanic and isothio-cyanic esters.

The remainder of the tests will give results that will be sufficiently obvious if positive results are obtained.

DETECTION OF ALKALOIDS.

These are optically active solids (Nicotine and coniine liquids) with bitter tastes and mostly poisonous. They are bases, rather insoluble in water, but forming soluble salts in acids, from which NH_4OH reppts. them.

Note.—Solutions of quinine sulphate, nitrate, phosphate and acetate show a blue fluorescence, destroyed by HCl.

Apply the following tests to the alkaloid to be identified.

1. Add either iodine in KI, potassium mercuric iodide soltn. or phosphomolybdic acid—all give ppts. Amm. molybdate in conc. H_2SO_4 gives colorations.
2. To a portion of the dry substance on a white tile add strong HNO_3.
   An orange-red colour, destroyed by $Na_2S_2O_3$ or $SnCl_2$ - = *Morphine.*
   An intense red colour, turned violet by $Na_2S_2O_3$ or $SnCl_2$ = *Brucine.*
   No colour - - - - - - - - - *Strychnine, Quinine.*
3. To a portion of the dry substance on a white tile add pure H_2SO_4 followed by a small crystal of $K_2Cr_2O_7$.
   A green colour - - - - - - - - - = *Morphine.*
   A blue colour, changing quickly to orange - - - = *Strychnine.*
   A violet colour - - - - - - - - - = *Quinine.*
4. To the dilute faintly acid solution of the alkaloid add bromine water followed by ammonia till alkaline.
   A green colour, changed to red by acids - - - = *Quinine.*
5. To the neutral or faintly acid solution add conc. chlorine water.
   White ppt. soluble in HCl - - - - - - - = *Coniine.*
   Red colour, changed to yellow-brown with conc. NH_4OH = *Brucine.*
   No colour, changed to intense green with conc. NH_4OH = *Quinine.*
   No colour, changed to yellowish white ppt. with conc. NH_4OH - - - - - - - - - = *Cinchonine.*

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DETECTION OF SIMPLE CARBOHYDRATES.

The solution of the suspected carbohydrate in water is neutralised or made slightly acid with HCl, and a little iodine solution in KI added to a portion.

- **Blue colour.** Starch.
- **Red colour.**
  - **Clear solution.** Erythrodextrin.
  - **Opalescent solution.** Glycogen.
- **No colour.** Sugars. Heat with Fehling's Solution.
  - **Reduction occurs.** Dextrose, maltose, lactose, fructose, galactose, pentoses. Distil some with strong HCl.
    - **Furfural is obtained in the distillate.** (Test with aniline acetate paper, which develops a bright pink colour with furfural.) Arabinose or other pentose. Confirm with phloroglucinol. (See p. 377.)
    - **No furfural.** Warm with Barfoed's reagent) (4% copper acetate with 1% acetic acid).
      - **Reduction.** Dextrose, fructose, galactose. Apply the mucic acid test.*
        - **No result.** Dextrose, fructose. Apply Seluvanoff's test.†
          - **Positive.** Fructose.
          - **Negative.** Dextrose.
          - Cf. by osazones.
        - **Mucic acid produced.** Galactose.
      - **No reduction.** Lactose, maltose. Apply the mucic acid test.*
        - **No result.** Maltose.
        - **Mucic acid produced.** Lactose.
        - Cf. by osazone.
  - **No reduction.** Cane sugar. Invert by boiling some with dilute HCl, neutralising and again testing.
    - **Reduction.** Sucrose.
    - **No reduction.** No carbohydrate present.

---

* If 1 part of the sugar and 12 parts of HNO_3 (S.G. 1·15) be evaporated to 2 parts in a porcelain basin, mucic acid may be produced, appearing as a white ppt. in a clear solution.

† Dissolve 0·05 gm. of resorcin in 100 c.cs. of dilute (1 : 2) HCl. Add the sugar solution to 5 c.cs. of this and boil. Red colour and red ppt. soluble in alcohol indicates fructose. *Prolonged boiling* gives the test with maltose and dextrose.

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PART II.

QUANTITATIVE ANALYSIS.

A. Estimation of the Elements.

1. *Determination of carbon and hydrogen* [nothing else but oxygen present].

Liebig's method.—The substance is completely oxidised by burning with copper oxide and the water and carbon dioxide are separately absorbed and weighed.

The apparatus required.—1. A combustion furnace about 80 cms. long provided with about 24 bunsen burners.

2. A hard glass combustion tube open at both ends, 10 cms. longer than the furnace, and about 15 mm. external diameter. One end is closed with a rubber stopper carrying a glass tap. The tube is fitted as shown in Fig. 99.

FIG. 99.

(*a*) A roll of oxidised copper gauze.

(*b*) Boat containing the substance to be burnt (sealed tube for liquids).

(*c*) Another small roll of oxidised copper gauze.

(*d*) A layer of pure copper oxide (made from copper wire clippings) about 45-50 cms. long.

(*e*) Another small roll of oxidised copper gauze.

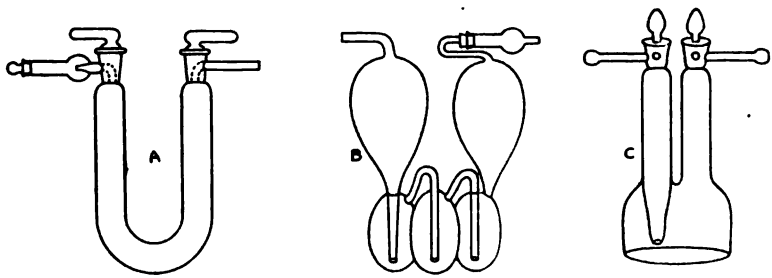

FIG. 100.

3. The calcium chloride tube. This is U-shaped and connected *directly* to the combustion tube by a rubber stopper (Fig. 100 (A)). The limbs of the U are preferably sealed off after filling the tube. The reagent is kept in place

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with small plugs of glass wool, and after filling, dry carbon dioxide should be passed through it for 15 minutes to destroy any basic chloride (which would absorb CO_2 in the determination) and then dry air to remove the CO_2. A tube will last for several determinations without refilling if the side tubes are closed with rubber tubing and short pieces of glass rod.

4. The potash bulbs (Fig. 100 (B)) to absorb carbon dioxide. Various forms are on the market. That shown is Geissler's. The guard-tube contains calcium chloride to prevent loss of moisture and is weighed with the bulbs. The bulbs contain concentrated potash (*not* caustic soda) 3 parts KOH : 2 parts water.

During an experiment another guard-tube containing calcium chloride is added to prevent the entrance of atmospheric moisture. This tube is *not* weighed.

5. The porcelain boat or small stoppered tube to contain the substance (solid or liquid respectively).

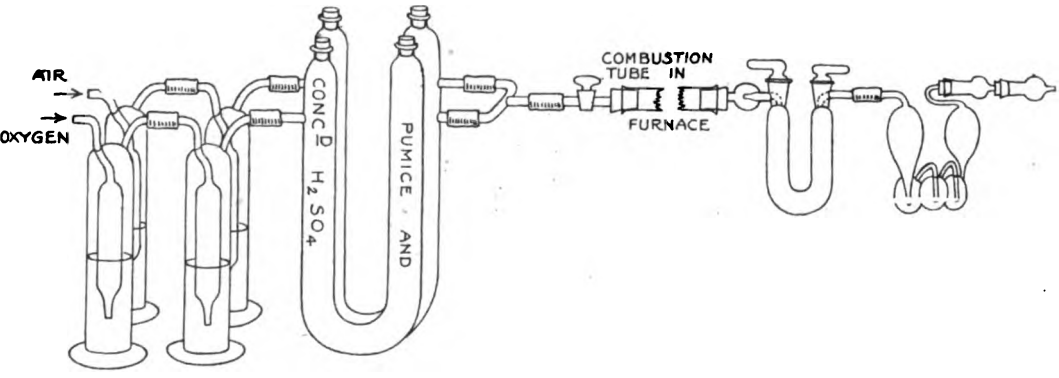

FIG. 101.

6. An asbestos board to protect the absorption tubes from the heat of the furnace.

7. A supply of air and of oxygen, in suitable aspirators or gas holders; each supply is provided with a purifying train to absorb moisture and carbon dioxide. (A tower of soda-lime followed by 2 U-tubes of pumice and strong sulphuric acid.) These are connected to a T-tube, which in turn is connected to the glass-tap of the combustion tube. Air or oxygen at will can thus be passed through the latter. The fully-equipped tube is shown in Fig. 101.

The operations.—The tube is filled as described and placed in the furnace. A stream of dry air is passed through it (5 bubbles per second) and it is heated to dull redness. The moisture which copper oxide always contains is thus driven off and is removed from the open end of the combustion tube by a roll of filter-paper. After half an hour the combustion tube is closed with a rubber cork carrying a guard-tube of calcium chloride to prevent ingress of atmospheric moisture, and the glass tap at the entrance end is closed.

Whilst the tube is cooling the calcium chloride tube and the potash bulbs are weighed, first removing the caps and leaving in the balance case for 10

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minutes. The boat (or stoppered tube) previously heated, is also weighed, and about 0·2 gm. of the substance weighed into it.

The stopper at the entrance end of the combustion tube is now removed, the roll of copper oxide gauze pulled out by the stout hook with which it is provided, the boat pushed into place, the gauze replaced and the stopper is put back into the tube. The guard-tube at the exit end is removed and the weighed calcium chloride tube takes its place. The potash bulbs are next attached, and finally the guard-tube (Fig. 1). Now turn on the air supply so that about 2 bubbles per second pass through the potash bulbs. All is now ready for

The combustion.—Having fixed the asbestos board in position to protect the absorption train, light the burners under the long layer of copper oxide (small flames at first), commencing at the exit end of the tube and gradually extending to the other end of the layer. Then light one or two burners under the roll of gauze at the entrance end of the tube, and finally under the boat itself. The more slowly the substance in the boat is vaporised and burnt the better; many substances, *e.g.* naphthalene, will readily pass over the whole layer of red hot oxide and condense unaltered in the calcium chloride tube if heated too quickly.* It is best to heat the boat at first by bringing some of the hot tiles near to it. Finally the whole furnace is brought to a dull red heat. Watch the bubbles in the potash bulb continually and keep the rate to 2 per second.

Any water condensing near the exit end of the tube is driven over by warming it by a hot tile held closely underneath it.

When combustion is complete (except for carbon in the boat), replace the air by an oxygen stream. Continue this till oxygen issues from the apparatus. (Test with a red-hot splinter held at the exit of the guard-tube.) Then replace the oxygen by air again, and finally turn out the burners. Remove the absorption tubes, put on the caps, and place in the balance case for at least 15 minutes. Wipe carefully with a clean dry silk cloth, and remove the caps immediately before weighing.

The percentage of carbon is obviously given by

$$\frac{3}{11} \times (\text{weight of } CO_2) \times \frac{100}{w},$$

and that of hydrogen by

$$\frac{2{\cdot}02}{18{\cdot}02} \times (\text{weight of water}) \times \frac{100}{w},$$

$$(w = \text{weight of substance taken})$$

that of oxygen being determined by difference.

The empirical formula of the substance can now be found in the usual manner.

* A substance particularly difficult to burn may be mixed in the boat with finely powdered copper oxide (dried at a red heat). This oxide must *not* have been made from copper nitrate.

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Modifications of this method necessitated by the presence of nitrogen, sulphur and halogens.

When nitrogen is present, oxides of nitrogen may be produced which would be absorbed by the potash and weighed as CO_2. To avoid this, a *freshly reduced* roll of copper gauze is added to the contents of the tube. This should be at least 10 cms. long and comes nearest the exit end of the tube, next to the calcium chloride tube. Oxides of nitrogen are thereby reduced.

Preparation of the copper gauze.—A large boiling tube and a cork to fit it *loosely* are taken. One or two c.cs. of pure methyl alcohol are placed in the tube, the copper gauze is heated to redness. Hold the boiling tube in a cloth, slide in the red-hot spiral. The alcohol vapour reduces the copper oxide to copper, and the vapour of the boiling alcohol takes fire at the mouth of the tube. When this flame goes out, cork the tube loosely. When cool take out the gauze and dry it by warming gently in a tube in a current of dry nitrogen or carbon dioxide. Cool it in the same current and cork it up until ready for use.

This copper spiral will take the place of some of the copper oxide layer in the combustion tube. The substance in the boat should be covered (after weighing) with pure dry copper oxide.

The combustion is the same as before, but do not use oxygen till the combustion is as complete as possible with air. Before turning on the oxygen, turn out the burners under the copper gauze.

When sulphur and halogens are present the copper oxide is replaced by fused and granulated lead chromate, as copper sulphate would not be stable at the temperature of the furnace, and sulphuric acid, sulphurous acid, traces of halogen and halogen acids would come over and be weighed as carbon dioxide.

It is important not to use too high a temperature when lead chromate is employed, or it will fuse into the glass and break the latter.

A roll of silver gauze placed at the exit end of the tube will arrest halogens with more certainty, and should be used if available.

Dennstedt's method of combustion.—The principle of this process is to bring the vapour of the substance, mixed with oxygen, into contact with red-hot platinum. A six-rayed star of platinum foil about 10 cms. long is employed as the most suitable contact agent. A great advantage of the method is that no special furnace is required, four burners being ample. The saving of gas is considerable. Nitrogen, sulphur and the halogens can also be estimated, the former by Dumas' method (see below) the latter by absorption in gently-heated (300°) lead peroxide. The method has been brought to a degree of refinement and simplicity impossible with Liebig's method, and if the necessary apparatus is available the student should carry out the experiments. After acquaintance with Liebig's method, Dennstedt's apparatus will be readily understood. It may here be mentioned that the greatest difficulty with which Dennstedt had to contend was the formation of explosive mixtures of the vapour with oxygen. This was finally overcome by the use of a double oxygen supply through two concentric tubes. The inner tube contains the substance, and a very limited supply of oxygen passes through it, just sufficient to carry

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forward the vapour. The main oxygen stream passes through the outer tubes and meets the other stream and the inflammable vapour at the platinum "star." The combustion should be carried out slowly to avoid incomplete combustion.

It may also be mentioned that Dennstedt has devised new and convenient forms of calcium chloride and soda-lime absorption tubes. (See Fig. 100 (C).)

These, the whole apparatus, and improved forms of electrically heated furnaces for the method may be found in the trade catalogues.*

Estimation of Nitrogen.

(1) **Dumas' method.**—The combustion is similar to that of Liebig, but the operation is carried out in a current of carbon dioxide, and the nitrogen evolved is collected over potash (*not soda*), measured and its weight calculated.

As oxygen cannot be employed, it is necessary to mix the substance intimately with finely-powdered pure copper oxide (*not* from copper *nitrate*) to ensure its complete combustion.

The various parts of the apparatus are as follows:

(1) A CO_2 generator. Various methods are used, but the most convenient is a large Kipp. No particular precautions as to drying the gas (or the copper

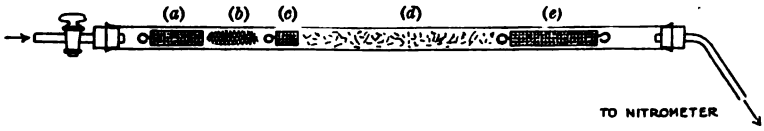

FIG. 102.

oxide) are absolutely necessary, but it is well to pass it through a wash-bottle containing sulphuric acid to prevent moisture carried over mechanically from cracking the tube, and also to see the rate at which the gas is passing. It will be necessary to test the gas and see that it is free from air. (See below.)

2. The combustion tube fitted as shown in Fig. 102.

(*a*) Copper oxide gauze roll, 12-15 cms.

(*b*) Intimate mixture of finely-powdered copper oxide and substance.

(*c*) 1 cm. layer of fine copper oxide.

(*d*) 35 cm. layer of wire from copper oxide.

(*e*) Freshly reduced copper spiral to reduce oxides of nitrogen.

Note.—The approximate nitrogen content of the substance should be known and such a quantity taken that the nitrometer will not be much more than half full.

3. The nitrometer is shown in Fig. 103. The inlet tube is just closed by a mercury trap which prevents any possibility of the potash being drawn into the combustion tube. The reservoir contains 40 % potash.

It is preferable to have the top of the nitrometer fitted with a funnel as shown. The nitrogen can then be transferred to a graduated tube and measured over water, of which the vapour pressure is known. That of the potash solution is not accurately known.

* See Messrs. Gallenkamp & Co.'s catalogue.

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The combustion.—The tube being charged and placed in the furnace, carbon dioxide is passed rapidly through it to drive out air. After about 15 minutes the nitrometer is attached. The gas stream is continued until the bubbles are completely absorbed by the potash. Any bubbles that have collected in the nitrometer are driven out by raising the reservoir and opening the tap. This is repeated till no more bubbles collect. Then diminish the rate of the CO_2 stream and commence to heat the tube, starting from the exit end and gradually approaching the substance as before. When most of the nitrogen has come over, increase the rate of the CO_2 stream. During the whole experiment maintain the potash reservoir at about the level of liquid in the graduated tube. When the volume of nitrogen no longer increases, disconnect the nitrometer, fix the funnel on the top and fill it with freshly-boiled cold water; bring a graduated gas tube full of the same water over the end of the nitrometer, and by raising the potash reservoir and opening the tap, drive the nitrogen into the tube. Transfer it to a glass cylinder full of air-free water and leave it for 15 minutes to attain the same temperature. Finally, holding the tube in a clamp (*not* with the hand) raise it till the water levels inside and outside are the same, and read the volume and the temperature of the water. Read the barometer and calculate the weight of nitrogen obtained.

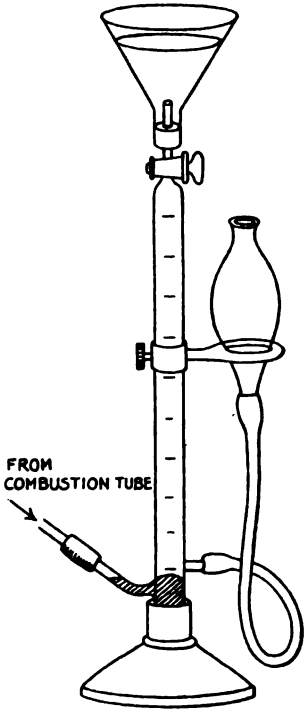

FIG. 103.

Example.—Let the volume of moist nitrogen obtained be v c.cs. at $t°$ C. and P mms. pressure. Then if f = the vapour pressure of water at $t°$, the volume V_0 at N.T.P. is

$$V_0 = \frac{v \times 273 \times (P-f)}{(273+t) \times 760}.$$

Since 1 c.c. of dry nitrogen at N.T.P. weighs ·001259 gms., the weight of nitrogen in the amount of substance taken is given by

$$V_0 \times \cdot 001259.$$

Before another determination is carried out it is necessary to re-roast the copper oxide, to reduce afresh the copper spiral and to replenish the potash. When the nitrometer is left, all the potash should be removed, the apparatus well washed with water and the tap slightly greased with vaseline.

(ii) **Kjeldahl's method.**—The substance is heated with strong sulphuric acid till the liquid, which chars at first, becomes clear.

By this means the nitrogen is converted to ammonium sulphate, from

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which the ammonia is driven by alkali into a known volume of standard acid. The excess of acid is then titrated with standard alkali.

It should be noted that with hydroxylamine and diazonium compounds and phenyl hydrazine derivatives no known modification of Kjeldahl's process will give accurate results, and the same is true if chlorides and nitrates are present together. With these exceptions, the modifications introduced by Gunning and Jodlbauer enable one to determine nitrogen in any other form of combination.

Fig. 104 shows the heating flask (of hard glass) while Fig. 56 gives one form of apparatus complete with the exception of a tap funnel fitted to the flask. The delivery tube should be made of Jena or equivalent glass, or best of silica, as freshly-distilled water containing ammonia dissolves appreciable amounts of alkali from ordinary glass.

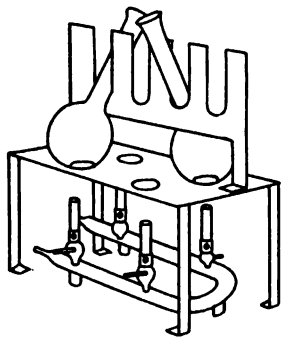

FIG. 104.

The experiment is carried out as follows:

Into a round-bottomed flask of 300 c.cs. capacity, with a long neck, a suitable weight of the substance is introduced.* About 15-20 c.cs. of pure sulphuric acid are poured in, about 10 gms. of dry potassium sulphate (or better 2 gms. of sodium pyrosulphate) are added, and the flask placed on its stand (with the neck inclined to the vertical) in the fume-cupboard. The contents are now boiled gently till the liquid, which chars at first, turns practically colourless again. The object of the sulphate is to raise the boiling point of the acid and hasten the operation.

After cooling, *carefully* dilute the contents with about 80-100 c.cs. of distilled water. Then the flask is fitted with a rubber cork carrying the tap funnel (not shown in Fig. 56) and delivery-tube. The stem of the tap-funnel should be drawn out to a point, and should not dip into the liquid in the flask at any stage. The delivery-tube is flush with the stopper. The trap prevents drops of alkali being carried over mechanically, and the bulb prevents any possibility of sucking back. (A 50 c.c. pipette with a wide nozzle is excellent.) Cool the receiver in a water-bath. When all is ready run a suitable amount of $\frac{N}{5}$ acid (50 c.cs. at the most) into the receiver, and through the tap-funnel run very carefully a suitable amount of 20 % caustic soda solution (80 c.cs. will be ample for 10 c.cs. of sulphuric acid). Then distil for 20-30 minutes. It is advantageous to add a few gms. of zinc dust with the caustic soda; this prevents bumping.

Finally titrate the excess of acid with alkali of known strength with litmus or methyl orange as indicator. (Not phenolphthaleïn.) Each c.c. of $\frac{N}{10}$ acid = ·001401 gm. of nitrogen.

* Use such an amount that about 25 c.c. of $\frac{N}{10}$ acid will be neutralised by the ammonia liberated.

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Gunning adds about 0·5 gm. of mercuric oxide or mercury to the strong sulphuric acid, as this lessens the time necessary for digestion. The mercury is pptd. by adding 25 c.cs. of 4 % potassium sulphide solution with the caustic soda before distilling.

In case nitro-compounds, nitrates, azo-bodies and amino-azo-bodies are present, the *Jodlbauer* modification is necessary. This consists in mixing 1-2 gms. of zinc dust with the substance, and dissolving 2 gms. of salicylic acid in the sulphuric acid before adding it to the substance. The acid is then poured quickly into the flask so as to cover the mixture of substance and zinc at once. (*B. Dyer.*)

Estimation of halogens, sulphur and phosphorus.

1. **Carius' methods.**—The substance is heated in a bomb-tube with strong nitric acid, being thereby completely oxidised. Halogens are converted to silver halide by the presence in the tube of silver nitrate. Sulphur and phosphorus are converted to sulphuric and phosphoric acids. After the operation is finished the remainder of the determination is carried out exactly as described in Gravimetric Analysis.

The bomb-tube is made of glass sold for the purpose. It is either of Jena (or equivalent) hard glass or of very thick-walled soft glass. It is closed at one end and, at the commencement, open at the other. It is about 35 cms. long, 2-3 mm. thick and 16-18 mm. diam. 0·1-0·2 gm. of the substance is introduced in a weighing tube, about 7 cms. long, 7-9 mm. diam., sealed at one end. After weighing the substance in it, the tube is placed in the bomb-tube, into which about 1-2 c.cs. concentrated fuming nitric acid (S.G. 1·5), free from halogens have been placed (see Inorganic Preparations), together with about 0·5 gm. of pure silver nitrate crystals, if halogen is being determined. This is omitted if sulphur or phosphorus are being sought. Do not allow the acid to come into contact with the substance till the tube is sealed. To seal the tube, warm it gradually in the blow-pipe flame and attach a piece of glass rod to the open end, by which to hold it. Then heat the upper end of the tube, about an inch from the end, turning it constantly in the flame and allow the glass to thicken somewhat. Carefully draw it out into a capillary (first removing it from the flame), and cut off the drawn-out portion some 3 inches above the shoulder. Now heat again just above the shoulder till the walls thicken, finally sealing it off by drawing off all but about an inch of the capillary. Anneal by gradually turning off the blast, holding the heated part in the smoky flame and finally allow to cool. Bring the contents into contact and place in the bomb-furnace (Fig. 105) in the iron tube which is lined with asbestos. The capillary should just project from the furnace. Turn the furnace to face a wall so that no damage may be done by an explosion. (A good plan is to have a heavy wooden board some 2 inches thick fixed in front

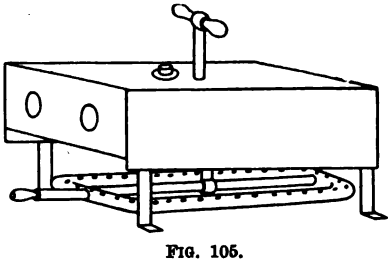

FIG. 105.

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of the furnace so that it inclines to the wall and the floor. All danger of flying splinters of glass is thus obviated.

Light the furnace and raise the temperature to the desired level (not more than 340° is ever necessary). Start the heating in the morning, continue till evening and leave to cool overnight. *Do not touch the bomb-tube from now onward until it has been opened.* This is carried out as follows. The tip of the capillary (projecting from the furnace) is brushed carefully with a small flame until the liquid which always condenses there has been driven out. The *tip* of the capillary is now melted in the flame; the pressure will then blow off when the glass is sufficiently soft.

It may now be safely handled, and is removed, cut off below the collar by making a file-mark round it and touching this firmly with a stout red-hot wire. Transfer the contents to a beaker, washing out several times with distilled water and carry on as usual. Before determining sulphuric acid evaporate off most of the nitric acid.

Though Carius' method is here described as being the classical method, that of **Stepanow, modified by Bacon** (*B.* 1906, **39**, 4056; *J.Am. C.S.*, 1909, **41**, 49) is far more convenient and is coming into general use.

Let *w* be the weight of substance employed. It is dissolved in the following quantities of 98 % ethyl alcohol, according as the halogen is chlorine, bromine or iodine, and the given quantities of sodium are used.

Halogen.	*Volume of alcohol.*	*Weight of sodium.*
Chlorine - - -	156 *w* c.cs.	19·5 *w* gms.
Bromine - - -	68 *w* ,,	8·5 *w* ,,
Iodine - - -	44 *w* ,,	5·5 *w* ,,

The alcohol and substance are placed in a flask fitted with a reflux (about 0·2 gms. of substance is recommended) and boiled. The sodium is added in small quantities at a time, the addition extending over not less than half an hour, and then boiling is continued for an hour. Allow to cool to about 50°, add water through the condenser, then nitric acid till acid. Finally add an excess of standard silver nitrate and titrate the excess by Volhard's method.

Pringsheim (*B.* 1908, **41**, 4267) mixes the substance with excess of sodium peroxide in an iron crucible, cools this in a bowl of water and starts the reaction by a red-hot iron nail introduced through a hole in the lid. Certain quantities of peroxide are used according to the carbon content of the substance. The method is unsuited for the student, though rapid and convenient.

Brunner estimates chlorine by liberating it by treatment with permanganate and concentrated persulphate solutions, determining it iodometrically as described in Volumetric Analysis.

Determination of metals.—(*a*) Compounds of silver, gold and platinum leave the metal when ignited in air.

(*b*) Compounds of lead, copper, etc., are weighed as oxide after ignition in air and treatment with nitric acid if necessary to reoxidise any reduced metal.

(*c*) Sodium and potassium compounds leave the carbonates when ignited. These may be dissolved and titrated with standard acid.

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Determination of molecular weights. (*For Physical methods see Physical Chemistry, Book VI.*)—Some special chemical methods for organic acids and bases will now be described. These are:

I. Direct titration.

II. Ignition of the silver salt of an acid or the platinichloride of a base.

III. Ignition of the alkali or alkaline earth salt of an acid and determining the residue volumetrically.

In all these cases we need to know basicity of the acid (or the acidity of the base). This may be found as follows:

(*a*) By neutralising the acid with soda or potash and preparing as many different salts as possible with 1, 2, 3, etc., equivalents of acid. This is not always conclusive, as in the case of oxalic acid, for example, we have $K_2C_2O_4$, KHC_2O_4 and KHC_2O_4, $H_2C_2O_4$.

(*b*) By finding the molecular weight by physical methods and determining chemically the number of replaceable H atoms in this weight. This may be done as described below.

(*c*) By determining the conductivities of the sodium salt λ_{32} and λ_{1024}. Ostwald showed that $\lambda_{1024} - \lambda_{32} = 10\ n$, where n = basicity. (See Physical Chemistry, Book VI.).

The molecular weight being known, the number of replaceable H atoms may be found thus:

$$NaHS + HX = H_2S + NaX,$$

i.e. 1 gm.-atom of acid hydrogen liberates 22·32 litres of H_2S at N.T.P.

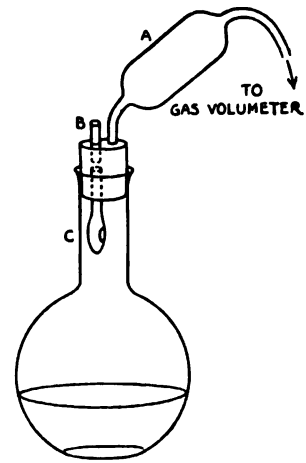

FIG. 106.

Thoroughly saturate some caustic soda solution with hydrogen sulphide (No Na_2S must be left or the results will be useless). A sufficient quantity (50 c.cs.) is introduced into the apparatus shown and a known weight of the acid is dropped into it by the arrangement in Fig. 106. The H_2S evolved pushes an equal volume of *air* through the delivery tube; this is measured gas volumetrically as described under Gas volumetric determinations, Book III.

In Fig. 106 (*a*) is shown a bulb of about 100 c.cs. capacity to prevent H_2S from reaching the water in the nitrometer.

(*b*) is a short glass rod to push (*c*) into the sulphide solution.

(*c*) is a small glass bulb-tube in which 0·2-0·4 gm. is weighed.

Having found the basicity the molecular weight may be found by:

I. **Titration** (see Volumetric Analysis).—Use standard baryta and dissolve the acid in CO_2-free water. Use phenolphthaleïn as indicator. The calculation will be sufficiently obvious, since the weight which neutralises a litre of $\frac{N}{10}$ baryta is $\frac{1}{10}$ of the equivalent weight of the acid. If this weight is found to be w gms., then the molecular weight is $n \times 10\ w$, where n is the basicity.

II. (*a*) **Ignition of the silver salt of an acid.**—Prepare the silver salt of the acid by neutralising the acid with ammonia, boiling off excess and adding

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silver nitrate to the cold solution. Filter at the pump, wash with cold water and dry in the steam-oven (in the dark).

Meanwhile strongly heat a porcelain crucible. Cool in a desiccator and weigh it. Weigh into it from 0·5-1 gm. of the silver salt and heat, *very* carefully with lid on at first, finally very strongly with lid removed, till nothing but metallic silver is left. Cool in a desiccator and weigh.

If the basicity of the acid is n, then, since the atomic weight of silver is 107·88, the molecular weight of the silver salt will be that weight which contains 107·88 n gms. of silver. Call this M. Then obviously $M - 107{\cdot}88n + n$ will be the molecular weight of the free acid.

II. (*b*) **Ignition of the platinichloride of a base.**—Prepare the platinichloride of the base by adding 10 % chlorplatinic acid to the fairly concentrated solution of the *hydrochloride* of the base. Filter, wash and dry at 100°. Ignite a weighed quantity to platinum in a porcelain crucible, just as described under the silver salt of the acid in the previous experiment.

The formula of the platinichloride is $B_2H_2PtCl_6$, BH_2PtCl_6, etc., according as B is a mono, etc., acid base.

(As regards the atomic weight of platinum to be taken, the "apparent" atomic weight of the platinum in the chlorplatinic acid used should be determined by preparing a chlorplatinate of a base of known molecular weight (say ammonium) and calculating the atomic weight from an ignition of a known weight of this).

III. **Ignition of the barium, calcium, sodium or potassium salt of the acid.** (The two former are often sparingly soluble and can be pptd.).—Prepare some of the required salt; dry it at 110°-130° and ignite a weighed quantity in a platinum crucible. The residue of oxide or carbonate may either be weighed (if pure) or, better, dissolved in excess of standard acid and the excess titrated. The method of calculation should be sufficiently obvious.

B. ESTIMATION OF VARIOUS RADICALS.

1. **Determination of hydroxyl** (alcoholic).—The hydroxyl groups are acylated either by boiling under a reflux with sodium acetate (anhydrous) and acetic anhydride, and pouring the product into water, or by the Schotten-Baumann method (p. 384) by shaking with 10 % caustic soda solution and excess of benzoyl chloride. The excess of acyl chloride is destroyed by warming with more caustic soda and the benzoyl derivative purified.

A known weight of the acylated product is then hydrolysed by boiling with alkali of known strength under a reflux (see p. 280). The excess of alkali is finally titrated. A simple calculation will give the number of acyl groups in 1 mol. of the acylated compound, provided that its molecular weight is previously known. Hence follows the number of hydroxyl groups in the molecule of original substance.

Hibbert and Sudborough (*J.C.S.*, 1904, **85**, 933) describe a simple method whereby the hydroxyl compound is treated with excess of magnesium-methyl-iodide in *absolute* amyl ether, and the volume of methane evolved measured by means of a nitrometer as described in gasometric determinations, Book III. The preparation of magnesium methyl iodide has been given, so that the

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student can easily carry out the determination without further instructions. Use about 0·2 gm. of the substance, 20 c.cs. of dry amyl ether and 15 c.cs. of the amyl ether solution of the reagent.

2. **Determination of methoxyl and ethoxyl. Zeisel's method** (*Monats.* **6**, 989 ; **7**, 406).—The body is heated with hydriodic acid and the evolved methyl iodide is caught in alcoholic silver nitrate and determined gravimetrically as AgI or volumetrically by Volhard's method. The apparatus is shown in Fig. 107.

A is a small flask containing about 0·3 gm. of the substance, 10 c.cs. of hydriodic acid (S.G. 1·7) and some pieces of porous plate to prevent bumping.

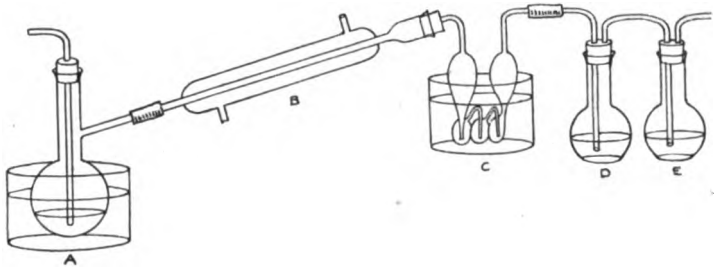

FIG. 107.

It is immersed in a glycerin bath and boiled, whilst a current of CO_2 passes through.

B is a Liebig condenser kept at 40°-50°.

C is a Geissler potash bulb immersed in a water-bath at 50°-60° for methoxyl, 80° for ethoxyl. This contains about 0·4 gms. of red phosphorus and some water to absorb hydriodic acid and iodine.

D and *E* are small flasks containing (*d*) 50 c.cs., (*e*) 25 c.cs. of alcoholic silver nitrate (2 parts of $AgNO_3$, 5 of water, 45 of absolute alcohol).

A is boiled for 1-2 hours till no more alkyl iodide is given off. The contents of *E* should be no more than slightly opalescent.

Finally wash out both *D* and *E* with about 500 c.cs. of water, evaporate to half-bulk on a water-bath, acidify with nitric acid and either weigh the pptd. AgI or determine the excess of silver nitrate by Volhard's method.

100 gms. of AgI ≡	19·21	gms. of	(OC_2H_5).
	12·34	,, ,,	(C_2H_5).
	13·2	,, ,,	(OCH_3).
	6·38	,, ,,	(CH_3).

3. **Determination of carboxyl, –COOH.**—The number of carboxyl groups in the molecule will be the same as the basicity of the acid, *q.v.* (p. 419).

4. **Determination of sulphoxyl, $-SO_3H$.**—Also by direct titration and a knowledge of the molecular weight.

5. **Determination of carbonyl, –CO–.**—(*a*) Free hydroxylamine is prepared by mixing hydroxylamine sulphate with baryta water in calculated proportions. The solution of the carbonyl compound in 50 % alcohol is made to react with a known excess of hydroxylamine, giving the oxime as already

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described (p. 315). Finally the excess of hydroxylamine is titrated with standard acid and methyl orange. From a knowledge of the molecular weight the number of oxime- and therefore of carbonyl-groups, follows at once.

(*b*) The weighed carbonyl compound is mixed with a known excess of phenyl hydrazine in aqueous solution. After the formation of hydrazone is complete the excess of phenyl hydrazine is titrated with $\frac{N}{10}$ iodine in the usual manner.

$$C_6H_5NH \cdot NH_2 + 2I_2 = 3HI + N_2 + C_6H_5I.$$

The phenyl hydrazine solution employed is estimated in the same manner.

6. **Determination of $-NH_2$ in primary amines.**—(1) By the platinichlorides as already described, p. 420.

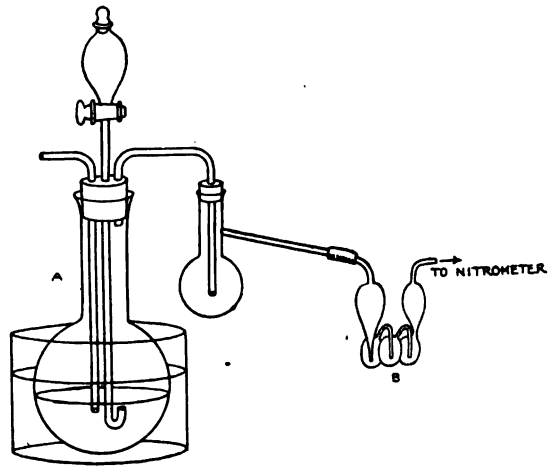

FIG. 108.

(2) By measuring the volume of nitrogen evolved when they are treated with nitrous acid. The nitrogen is swept into a nitrometer containing potash by means of a current of carbon dioxide.

A suitable amount of the substance is dissolved in dilute sulphuric acid and placed in flask *A*, Fig. 108, which is fitted as shown. The tap-funnel contains air-free distilled water at first. The potash bulbs *B* contain 3 % $KMnO_4$ containing 1 gm. of caustic soda, and are connected to a nitrometer as for Dumas' estimation of nitrogen, p. 414. The tube of the tap-funnel is filled with the distilled water. CO_2 is passed through the apparatus till all air is swept out, and then the flask is warmed on the water-bath. A solution of potassium nitrite containing a little potassium iodide is now run slowly into the flask from the funnel, keeping up the CO_2 stream throughout. When iodine is liberated in the flask sufficient nitrite has been added. Heat the water-bath and carry on the CO_2 stream till all nitrogen has been swept out. Measure it and calculate as in Dumas' nitrogen determination. Remember that only one half of the nitrogen comes from the amino-group.

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Aromatic amines are estimated in the above manner but at a gentle boil, but more conveniently by titrating the dilute (0·1 %) solution of the hydrochloride with $NaNO_2$ of known titre (see p. 249, Volumetric Analysis). The titration is carried out at 0°, and starch-iodide paper is used as the (external) indicator. Excess of nitrite turns it blue.

Other methods available are

(1) Transformation to halogen derivatives by Sandmeyer's reaction, and estimation of the halogen.

(2) Acylation of the amino-group and hydrolysis of the product.

(3) In the case of **aniline** itself, the estimation may be carried out by titration with bromine water of known strength (François, *J. Pharm.* 1899, 521).

$$C_6H_5(NH_2)+3Br_2=3HBr+C_6H_2Br_3(NH_2).$$

Note that as bromine water is weak, a *small* quantity of aniline should be taken or the titration will be very long and tedious.

Other substances which absorb bromine should of course be absent.

The indicator is a little indigo solution, which is bleached by the bromine only when the above reaction is completed.

Note.—1. If preferred, a solution of bromine in concentrated potassium bromide may be used.

2. Remember that bromine solution will rapidly weaken in contact with the air, owing to the evolution of bromine vapour. Avoid this by a plug of cotton wool in the burette.

3. Reinhardt (see *J.S.C.I.*, 1899, 110) employs a solution of $KBrO_3+5KBr$ as his brominating agent. This is made by adding bromine to potash solution (pure) and boiling till the liquor no longer reacts with starch-iodide paper.

The aniline must, of course, be present in *acid* solution for this method. Starch iodide paper is employed as external indicator.

4. Aniline *salts* of mineral acids may be titrated directly with standard alkali and litmus.

Determination of the Imino-Group, $>$NH (Reverdin and de la Harpe, *B.* **62**, 1005).

Example. **Methyl aniline.**—About 1 gm. is weighed into a flask with a reflux condenser and about 2 gms. of acetic anhydride dropped in through the condenser, by weighing out by difference from a stoppered vessel. Leave for 30 minutes, then add 50 c.cs. of water and heat on a water-bath for ¾ hour. Cool, dilute to a known volume and titrate the excess of acetic acid in an aliquot part, using $\frac{N}{10}$ caustic soda and phenolphthaleïn. Hence the *excess* of acetic anhydride may be found, the remainder being inactive as it has formed the acetyl body.

Vaubel (*J.S.C.I.*, 1893, **12**, 954) recommends the use of a 7 % solution of acetic anhydride in xylene as the acetylating agent. After standing for an hour, water is added as before and the acetic acid remaining is titrated.

In case both $-NH_2$ and $>$NH are present, the total nitrogen is obtained as above, the $-NH_2$ nitrogen by the previous method. The difference gives the imino-nitrogen.

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Determination of amido- and imido-groups, $-CONH_2$ and $-CO.NH-$.—Both of these are estimated by boiling with alkali and collecting the ammonia evolved in standard acid. The apparatus is similar to that for the Kjeldahl distillation of the ammonia.

Determination of the nitrile group, $-CN$.—This is determined by acid hydrolysis to the ammonium salt followed by distillation of the ammonia into standard acid as in Kjeldahl's method.

(1) Most nitriles are hydrolysed by boiling with strong hydrochloric acid (reflux) till they have gone into solution. Then they are made strongly alkaline and distilled.

(2) Some require alkaline or even alcoholic alkaline hydrolysis. In this case the apparatus is as for Zeisel's ethoxyl determination (p. 421). The bulbs in this case contain concentrated potash and the ammonia is driven out by a current of air into standard acid in the two absorption flasks.

Certain cases of steric hindrance have been studied by Hantzsch and Lucas (*B.* **28**, 748). In these cases acid hydrolysis is useless and prolonged alcoholic alkaline hydrolysis is necessary.

Determination of the nitro-group, $-NO_2$.—Aromatic nitro-groups are determined by reduction to amine with stannous chloride and titration of the excess of stannous chloride with $\frac{N}{10}$ iodine or permanganate. (Not applicable to picric acid, etc., or to nitro-naphthols.) (See Young and Swain, *J.C.S.*, 1898, ii. 186. Altmann, *J.pr. Ch.*, 1901 [2], 63, 370.)

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = \cdot 0059 \text{ gm. Sn} = \cdot 0007655 \text{ gm. } NO_2.$$

If the body is non-volatile, weigh out about 0·2 gm., and place it in a 100 c.c. glass-stoppered flask. Add 10 c.cs. of stannous chloride of known titre, titrated immediately before use. This solution is made by dissolving 30 gms. of granulated tin in strong hydrochloric acid, decanting from any residue, adding 10 c.cs. of pure hydrochloric acid and making up to 200 c.cs.

The amine and tin solution is warmed for half an hour, cooled, made up to 100 c.cs. and shaken. 25 c.cs. are transferred to a beaker, a solution of 10 % Rochelle salt and 9 % sodium carbonate added till the ppt. first formed redissolves, and the excess of stannous chloride titrated with $\frac{N}{10}$ iodine with starch as indicator.

Reactions : $R.NO_2 + 3SnCl_2 + 6HCl = R.NH_2 + 3SnCl_4 + 2H_2O$

$$2SnCl_2 + 2I_2 = SnCl_4 + SnI_4.$$

If the body is readily volatile, weigh it in a small corked test-tube. The cork is removed and the tube dropped into a small stoppered bottle containing the stannous chloride. The stopper is tied on securely and the bottle heated in a water-bath with constant shaking for 1-2 hours. When cool open and proceed as above. **For another method see pp. 219 and 274.**

Determination of diazonium bodies (Bamberger, *B.* **27**, 25, 98).—The nitrogen is driven off by boiling with dilute sulphuric acid in a small flask fitted with a reflux The top of the reflux is connected to a nitrometer as in

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gasometric determinations (Volumetric Analysis, p. 275). After adjusting the pressure to atmospheric, the solution is boiled and allowed to cool before final adjustment of the gas volume.

Hehner's method (*J. pr. Ch.*, 63 [27] (1091), 304) is also suitable for determining diazo-amino bodies. A test-tube about 3 × 10 cms. is fitted exactly as shown in Fig. 109. *E* is connected to a nitrometer filled with potash (as in Dumas' nitrogen determination), *A* to a CO_2 Kipp and *C* to an air-pump. *B* is drawn out to a point, and is filled with distilled water below the tap.

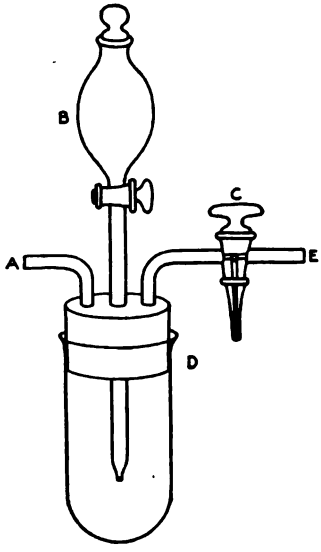

FIG. 109.

A weighed amount of the substance is placed in the test-tube and the tube exhausted. CO_2 is let in, exhausted again, and this is repeated several times. Finally the tube is filled with CO_2 and *C* closed. Now introduce some strong hydrochloric acid through the tap-funnel (do not let any air in); the liquid is boiled and the nitrogen evolved is collected in the nitrometer and measured in the usual manner.

Determination of iodoso and iodoxy groups, –IO and IO_2 (Willgerodt, *B.* **25**, 3495).—These, in the presence of acid, liberate iodine from potassium iodide in amount equivalent to their oxygen content. They are digested on a water-bath in a securely stoppered bottle with strong potassium iodide solution and some glacial acetic acid. Finally the liberated iodine is titrated with $\frac{N}{10}$ thio-sulphate.

$$\left.\begin{array}{l} RIO \text{ liberates } I_2 \\ RIO_2 \text{ liberates } 2I_2 \end{array}\right\} \text{from potassium iodide.}$$

Estimation of glucose (volumetrically).—1. *By Pavy's solution.*

Principle.—The glucose is oxidised to oxalic acid by a copper salt, which is reduced to Cu_2O with decolorisation. The presence of Rochelle salt and ammonia prevents the pptn. of Cu_2O.

Pavy's solution is made by dissolving 3·466 gms. of pure copper sulphate in 200 c.cs. of water and adding it to a solution of 20 gms. of Rochelle salt and 18 gms. of caustic soda in 200 c.cs. water. Now 300 c.cs. of ·880 ammonia are added and the whole made up to a litre.

$$1 \text{ c.c.} = \cdot 0005 \text{ gm. glucose.}$$

The exclusion of air is necessary during the titration, which is carried out at the boil. Standardise this solution against a known glucose solution.

Place 100 c.cs. of Pavy's solution in the flask, and exclude air *either* by fitting it with a cork, through which pass (1) the burette end, (2) an escape tube leading to a vessel of acid to absorb the ammonia, *or* by a layer of high boiling paraffin on the solution (Allen, *Commercial Organic Analysis*).

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Boil the liquid gently and add the sugar solution till the Pavy's reagent is just decolorised. This must take place before the ammonia has evaporated, yet not so quickly as to overshoot the mark, as the reaction is somewhat slow. Repeat more accurately after performing an approximate determination.

Cane sugar may be estimated in the same manner after inversion by boiling for 15 minutes with 2 c.cs. of strong hydrochloric acid and 100 c.cs. of water for each gram of sugar. After cooling neutralise the acid by adding soda. Make up to 100 c.cs. again and titrate as above.

1 c.c. Pavy's solution = ·000481 gm. invert sugar.

2. *By Gerrard's cyanide modification of Fehling's method.* The use of Fehling's solution alone is somewhat unreliable owing to rapid reoxidation of pptd. Cu_2O, but in Gerrard's method, pptn. is prevented and reoxidation hindered by means of a solution of the double cyanide of copper and potassium. This solution, which does not enter into the calculation though containing copper, is made by diluting say 100 c.c. of Fehling's solution (see below) with about 250 c.c. of water, boiling and adding a 5 % solution of KCN from a burette until the colour *just* vanishes. Cool and make up to 500 c.c.

Perform the titration, by taking 50 c.c. of this solution, in a large porcelain dish, and to it add 10 c.c. Fehling's solution previously standardised by this method against a known glucose solution.

Keep boiling and titrate with the solution to be determined from a burette until the colour vanishes. If necessary, dilute the unknown solution so that about 10-15 c.c. are required for the titration; the strength of the sugar solution should always be of this order.

The Fehling's solution is made up by mixing equal quantities of the two following solutions just before use, as the mixture does not keep:

First Solution.—Dissolve 34·66 gm. $CuSO_4 . 5H_2O$ in about 350 c.c. water, cool and make up to 500 c.c. (Keep clear with a drop or two (only) of dilute H_2SO_4 if necessary.)

Second Solution.—Dissolve 180 gm. Rochelle salt in about 300 c.c. water, add 75 gm. NaOH or about 100 gm. KOH after filtering, and make up to 500 c.c.

Since $C_6H_{12}O_6 \equiv 5CuSO_4 . 5H_2O$,
each titre of 10 c.c. mixture ≡ 0·05 gm. glucose or 0·06 gm. lactose.

Literature.

Most of the books quoted under Organic Preparations.
* Commercial Organic Analysis. ARUP. (Churchill.)
For tables of physical constants for organic compounds, see books of KAYE and LABY, LANDOLT-BÖRNSTEIN, or RICHTER'S Lexicon der Kohlenstoff verbindungen.

* An introduction to the commercial side.

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BOOK VI.

PHYSICAL CHEMISTRY.

INTRODUCTION.

CALCULATION OF RESULTS.

Calculation of results.—As in Physical Chemistry we rely largely upon the methods of physics for deducing laws, the subject is almost entirely quantitative and depends upon accuracy in working.

Errors are, of course, unavoidable, and may be classed into

(*a*) Constant errors.
(*b*) Experimental errors.

Constant errors can only be avoided by performing the experiment by many different methods; thus, the determinations of the atomic weight of Tellurium suffer from the fact that *possibly* another element is associated with it, and until the element is prepared from some source independent of this, the result must be inaccurate.

Experimental errors depend upon the sensitivity of the apparatus and the skill of the experimenter. If several experiments are performed, the mean will be very near the correct result.

The significant figure to which the result is carried depends on the least accurate reading; for example, it is manifestly useless to trouble about the third place of decimals when the accuracy of some determinations in the same series and of the same order is only carried to the first place.

If the numbers 1·2, 2·34, 4·567 be added, the accuracy of each number being tacitly represented by the number of places of decimals, the sum is only significant to the first place, though the next figure is often included.

Errors per cent. can be calculated and the results made consistent.

If two quantities, x and y, are proportional to one another, one being determined by means of the other, then if x varies as y, the *relative* error is the same in both, and if $x=ay$, the absolute error in y is a times that in x.

But if $x \propto y^2$, then $\frac{dx}{x}$ and $\frac{dy}{y}$ represent relative errors in x and y.

We have
$$dx=2ydy,$$
$$\therefore \frac{dx}{x}=\frac{2ydy}{y^2}=\frac{2dy}{y}$$

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so that the relative error in y is proportional to its index, and the absolute error in the above case to $dx = 2ydy$.

The probable error is known from the results; thus, if a series of results is 2·57, 2·55, 2·54 and 2·58, the mean is 2·56, the individual deviations are ·01, ·01, ·02, ·02, the average is ·015, so that the error of the determination is 15 in 2560 or 0·6 %.

Knowing the error expected, suitable logarithms should be used for working up the results—five figure logarithms have a possible error of about one in 30,000, seven figure logarithms of one in 1,000,000.

Apparatus.—The general apparatus by means of which determinations are made is chiefly that for determining mass, volume, and temperature. All measuring apparatus must be calibrated.

N.B.—The terms "weighing" and "weight" will be used in future; the student will appreciate the difference between mass and weight.

Measurement of weight.—This is the most accurate, and at the same time most general operation in obtaining results. Accurate results depend on the sensitiveness of the balance and upon the accuracy of the weights, which must be calibrated after determining the 'zero point' of the balance, or mean point about which the balance pointer swings.

If this zero point is more than two divisions from the centre, the adjustments of the balance must be altered and the process repeated.

Determination of the sensitiveness of a balance.—The sensitiveness may be increased by raising the small screw adjustment at the top, but as this increases the time of oscillation, care must be taken not to overdo it.

To determine the sensitiveness for a given load, place one of the given loads in each pan and note the zero point. Then increase the load on one side and again determine the resting point. From the difference the movement per milligram per load can be calculated.

Repeat with different loads and plot a graph shewing the sensitiveness in each case against the pan load.

This curve will serve to simplify weighings, interpolation giving intermediate readings.

Thus, if the zero point is +0·4 divisions (*i.e.* 4 divisions right) with a load of 5·356 grams, and with 5·357 grams it is −0·2, the sensitiveness for the load 5·356 as determined by the curve being 1·2, the true weight is

$$5{\cdot}356 \text{ gr.} + \frac{0{\cdot}6^{\text{(difference)}}}{1{\cdot}2} \text{ m.g.} = 5{\cdot}3565 \text{ m.g.}$$

The results should not be carried to too many places of decimals as they will have no meaning.

It is seldom that balance arms are sufficiently unequal in length to make any serious difference, particularly if the same pan be employed for the load each time.

Should an absolute weight or mass be required, the ratio of the arms being $\frac{R}{L}$ (R = right; L = left arm), (see below), then the weight $W = \frac{R}{L}w$, where w is the apparent sum of the "weights" in the right-hand pan.

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Calibration of the weights (*Kohlrausch's method*).—Take a full set of weights, '50,' 20, 10^1, 10^2, 5, 2, 1^1, 1^2, 1^3, and the fractions.

Put the '50' on one pan, and the others, totalling 50, on the other.

If they do not balance, place small weights on the lighter side until they do.

Thus, suppose

$$\text{'50'} = 20 + 10^1 + 10^2 + 5 + 2 + 1^1 + 1^2 + 1^3 + r \text{ mg.}$$

Transferring to the other pans,

$$20 + 10 + 10 + 5 + 2 + 1^1 + 1^2 + 1^3 + l = 50.$$

From these measurements, we know that if R and L are the effective lengths of the arms,

$$\frac{R}{L} = 1 + \frac{l-r}{100000},$$

and $$\text{'50'} = 20 + 10^1 + 10^2 + 5 + 2 + 1^1 + 1^2 + 1^3 + \tfrac{1}{2}(r+l) \text{ mg.}$$

Similarly we may compare the '20' with $10^1 + 10^2$,
10^1 with 10^2,
10^1 with $5 + 2 + \ldots$, and so on.

If relative weighings alone are required, we may assume the '50' to be correct; if absolute weighings are necessary, the '50' should be compared with a standard, and $\frac{R}{L}$ determined for different loads for future reference.

Thus: A. 50 (standard) = '50' + 0·0002 gm.
'50' + 0·0008 = 50 (standard).
∴ 50 (standard) = '50' + ½ (0·0002 + 0·0008).
= '50' + 0·0005 gm.
∴ '50' = 49·9995 gm.

B. '50' + 0·0012 = '20' + '10' + 10^2 + ...
'20' + ... = 50 + 0·0034.
∴ '50' = (20 + ...) + 0·0023.

Hence, in true weight,
'20' + ... = 49·9995 − 0·0023,
= 49·9972 absolute.

Finally, having found the differences between the lower weights, we obtain the absolute values of all the weights in turn.

Correction for air displacement.—Suppose the body being weighed has the density d, the brass weights having the density 8·5.

Then, if the weights total W gm., assumed true except for air displacement, the actual weight of these is

$$W + \frac{W}{8{\cdot}5}(0{\cdot}0012), \text{ taking air as } 0{\cdot}0012 \text{ gm. per cc.}$$

To the first approximation the volume of the body is $\frac{W}{d}$, and the weight is therefore

$$W + \frac{W \times 0{\cdot}0012}{d};$$

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∴ True weight as determined by the balance is

$$W + \frac{W \times 0{\cdot}0012}{d} - \frac{W \times 0{\cdot}0012}{8{\cdot}5}.$$

Hence for every gram, there must be added

$$0{\cdot}0012\left(\frac{1}{d} - \frac{1}{8{\cdot}5}\right), \text{ or } \frac{0{\cdot}0012}{d} - 0{\cdot}00014.$$

Corrections per gram.

Body of density	1	+1·06 mg.	7	+0·029 mg.
,,	2	+0·457 ,,	8	+0·007 ,,
,,	3	+0·257 ,,	9	−0·010 ,,
,,	4	+0·157 ,,	10	−0·023 ,,
,,	5	+0·097 ,,	13·6	−0·055 ,,
,,	6	+0·057 ,,		

Calibration of measuring instruments.—To calibrate a flask, weigh empty, then fill to the mark with distilled water and weigh again, noting the temperature. Allow for the air and reduce to vacuum standards. The volume corresponding to the apparent weight of one gram of water is then looked up from Tables. If the vessel be small, mercury is employed owing to the greater specific gravity, and therefore the smaller relative error in volume calculated from weight and specific gravity.

For further details regarding the calibration of pipettes, burettes, etc., see the section on *Quantitative Analysis*.

Determination of temperature.—The use of thermometers is dealt with in text-books of Physics, but a few general points are here raised.

Mercury thermometers are used in the vast majority of cases for temperatures up to 300° C., and they must be calibrated either by determining fixed points or by comparison with standard or air thermometers.

Useful fixed points are:

Melting points of ice and naphthalene.

Boiling points of ether, methyl alcohol, absolute alcohol, water, amyl alcohol, aniline, nitrobenzene, mercury.

The errors are determined (allowing for exposure of the stem) and plotted on a graph.

When thermometers are calibrated by comparison with a standard, the two are placed side by side in a liquid bath, the temperature being then raised slowly. The readings are recorded at each degree and the errors plotted as for burettes.

If the thread protrudes for n degrees of exposed stem, t_t being the true temperature and t_x the mean external temperature of the stem, a the coefficient of apparent expansion of mercury (0·000156), then the correction to be added is

$$n\,a(t_t - t_x).$$

N.B.—Thermometers accurately calibrated by the N.P.L. or Kew can be purchased.

Measurement of high temperatures (platinum resistance thermometer).—The resistance of a platinum wire varies almost linearly with the absolute temperature, though the exact relation is

$$R_t = R_o(1 + \alpha t + \beta t^2 + \ldots).$$

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At $-273°$ C. the resistance, judged from temperatures just above it, would be zero.

We can calibrate the thermometer by finding the values of α and β by measurements of the resistance at fixed temperatures, and so construct a curve which, by interpolation, will give us the relation at any temperature.

The platinum resistance thermometer consists of a thin platinum wire about one metre long wound around a mica cross into which niches are cut to hold the wire in position. It is carried down into its protecting porcelain tubes by means of thick copper leads, a dummy pair of leads not joined to the platinum wire being included to act as compensators.

Effects due to magnetic induction are avoided by winding the wire downwards and then doubling it back in a reverse spiral from the bottom upwards. (Fig. 110.)

The resistances of the leads and of the compensators are found; in a good instrument they should, of course, be equal.

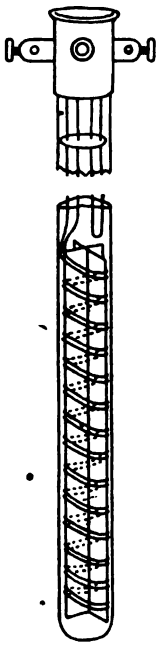

FIG. 110.

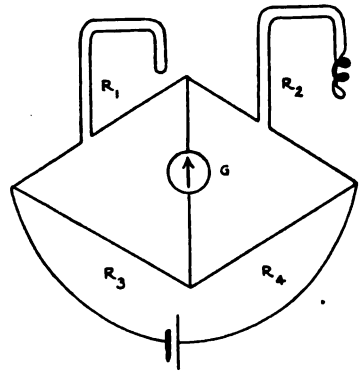

FIG. 111.

The resistance of the instrument is determined by means of a Wheatstone Bridge apparatus using a sensitive coil galvanometer. (See books on Practical Physics, also *Electro-Chemistry*, Chapter X.)

Referring to Fig. 111, if R be the resistance of the leads and platinum wire, R_3 and R_4 the resistances of the bridge arms and R_1 a variable standard resistance or Rheostat, then at the balance point

$$R_1 + \text{resistance of compensator} : R_3 :: R : R_4.$$

The increase in the resistance of the compensator after placing the instrument in a high temperature enclosure must be found and reckoned.

If a special apparatus be employed in which the compensator is placed as shown, R_3 and R_4 being *equal* standard resistances, and R_1 a Rheostat graduated in degrees and tenths of a degree (or less), the temperature on obtaining the balance in a galvanometer may be read off directly, as in this case the compensator neutralises exactly the effect of the leads.

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The Resistance thermometer may be employed for temperatures up to 1300° C. and down to −250° C.

Thermo-electric thermometers may also be used for determining temperatures, the E.M.F. generated being calibrated by fixed points with the aid of a sensitive galvanometer.

Thermostats.—Constant temperatures enclosures are termed thermostats. These may be divided into

1. Thermostats for Short Periods.
2. Thermostats for Indefinite Periods.

1. Short Period thermostats are obtained by the use of melting or boiling substances, or substances undergoing transition, *e.g.* melting ice packed

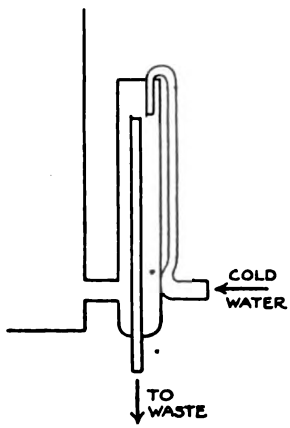

FIG. 112.

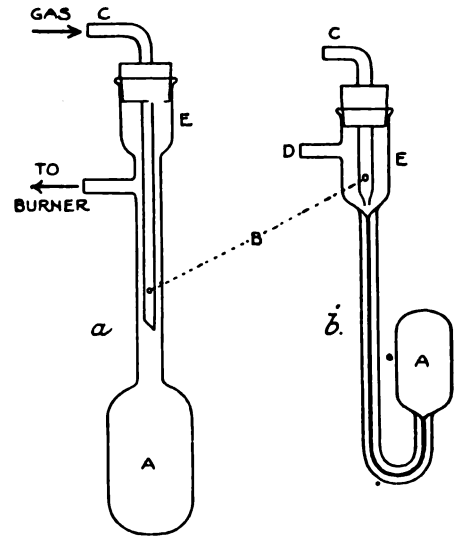

FIG. 113.

around the enclosure or water boiling in the outer portion of a double vessel, the water being kept constant in volume either by the attachment of an upright condenser to the vent tube or of a side tube device such as that shown in Fig. 112.

2. Indefinite Period thermostats require a regulator placed in the enclosure, also some stirring device.

A regulator, two forms of which are shown in Fig. 113, may be made very easily from a few pieces of glass tubing.

The bulb *A* is filled with mercury, toluene, aniline, or some convenient liquid with a high coefficient of expansion and sufficiently high boiling point. This is done by exhausting *A* by means of a pump whilst *D* is joined to a clipped rubber tube connected with a supply of the liquid. The clip is then opened, causing liquid to run in, the operation being repeated until enough has been introduced.

Finally, in (*b*), the capillary is filled with well cleaned mercury.

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To regulate the device, place in the thermostat, connect tube *C* to the gas supply, and *D* to the burner heating the thermostat. The temperature rises until the mercury is forced up the capillary closing the end of *C*. A small hole *B* in tube *C* allows sufficient gas to pass to maintain a tiny flame until the mercury recedes again.

By varying the height of *C* the required temperature may be obtained; for temperatures below 50° C. a small bunsen giving a luminous flame will suffice, but whenever a bunsen is used arrangement must be made for preventing any "striking back." An Argand burner is better.

The stirring arrangement is best given by means of vanes on a rod rotated by means of a pulley and belt attached to an electric motor or hot air engine.

Cleansing of mercury.—When mercury is amalgamated with an easily oxidised metal such as zinc, it may be purified by drawing a current of air through the liquid under a solution of mercurous nitrate acidified with a little nitric acid, when the zinc will oxidise.

Another method is to feed the foul mercury from a pin-holed filter-paper in a funnel through dilute nitric acid, and draw it off in the manner shown in Fig. 114.

With other metals it will be necessary to distil the carefully dried mercury, preferably under diminished pressure or in vacuo.

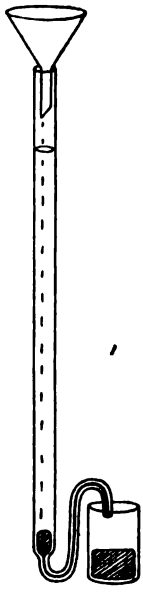

FIG. 114.

Vacuum pumps.—Details of these, *e.g.* the Sprengel and Toepler, occur in text-books of Physics.

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CHAPTER I.

DENSITY.

Definitions.

1. The *Density* of a body is the mass of unit volume.

2. The *Relative Density* is the mass of a certain volume of a substance compared with the mass of the same volume of a standard substance at the same temperature (and pressure in the case of a gas).

3. The *Specific Gravity* is the ratio of the mass of a certain volume of the substance compared with the mass of the same volume of water at 4° C. (the temperature of the maximum density of water).

4. The *Specific Volume* of a substance is the volume occupied by unit mass of the substance.

5. The *Molecular* and *Atomic* Volumes are the volumes occupied by the molecular and atomic weights of a substance respectively.

Note.—In the case of gases the density of hydrogen at the same temperature and pressure as that of the gas in question is taken as the standard.

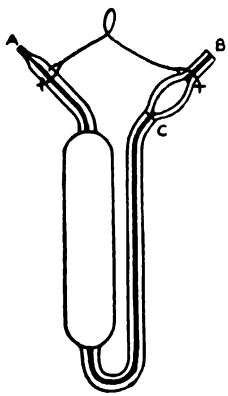

FIG. 115.

Symbols.—The symbols d and ρ are usually employed for denoting density, $d_t^{t'}$ signifying the density of a substance at t'° compared with that of water at t°.

(1) **Density of solids.**—The methods employed are dealt with in elementary books on mechanics. Summarised, they are as follows:

1. By determination of the mass and volume directly or by difference.

2. By the specific gravity bottle.

3. By Archimedes' Principle—weighing in air and water or other liquid.

4. By preparing a liquid in which the body will just float or sink, and finding the specific gravity of this.

(2) **Density of liquids.**—The density of liquids may be determined at ordinary temperatures, (*a*) by *hydrometers or the Westphal balance.*—See elementary books on Mechanics. (*b*) By *the pyknometer.*

The pyknometer is a small instrument with a bulb of about 5-15 c.c. capacity, and of the shape shown in Fig. 115 or similar thereto.

It can be made easily from capillary tubing, and is readily filled and cleaned.

The ends *A* and *B* are fitted with ground glass caps, or with loosely

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fitting caps which are simply pushed on. The bore of the capillary tubing should be about 1 mm.

To clean it, wash well with chromic acid mixture followed by (1) distilled water, (2) redistilled methylated spirit. Then draw a filtered current of air through it, warming in the steam-oven for some minutes while the air is passing.

It is necessary to wait for a considerable time (at least a day) to allow the volume to return to its constant value, but if this cannot be done the warming is not carried out. In this case another washing with redistilled ether is necessary, after which a current of clean air is aspirated through it.

When clean and dry, weigh the instrument empty by suspending it from the balance hook with a platinum wire, taking the weighing to the fourth place of decimals.

To fill, dip the end *A* under freshly distilled, air-free water, and with a rubber tube placed over the end *B*, suck until the bottom of the meniscus stands beyond the mark *C* in tube *B*.

Then suspend in a constant temperature bath for half an hour, after which, bring the meniscus exactly to the mark *c* by touching *a* with a filter-paper to extract water.

If too much is withdrawn, more must be introduced by bringing a drop of water into contact with *a* and tilting the pyknometer away from it.

When adjusted exactly, tilt the instrument so that the water leaves the end *a* and enters the bulb *c*; dry, place caps on the ends, stand in a beaker in the balance case until it has assumed the surrounding temperature, and weigh.

Finally, dry and repeat the operations with the liquid, the density of which is required.

If w be the weight of the water, w_1 that of the liquid at $t°$ C.,

then $$d_t^t = \frac{w_1}{w}$$

or $$d_4^t = \frac{w_1}{w} \times (\text{density of water at } t° = d).$$

Reducing to vacuum standard

$$d_4^t = \frac{w_1 d}{w} - \frac{0{\cdot}0012(w_1 - w)}{w}.$$

Table of densities of water at different temperatures.

Temperature.	Density.	Temperature.	Density.	Temperature.	Density.
0°	0·99987	10°	0·99973	20°	0·99823
1°	93	11°	63	21°	02
2°	97	12°	53	22°	0·99780
3°	99	13°	40	23°	56
4°	1·00000	14°	27	24°	32
5°	0·99999	15°	13	30°	0·99567
6°	97	16°	0·99897	40°	224
7°	93	17°	80	50°	8807
8°	88	18°	62	60°	324
9°	81	19°	43	70°	7781

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(3) **Density of a liquid at or near its boiling point.**—This may be done by Crompton's form of Ramsay and Lothar Meyer's pyknometer.

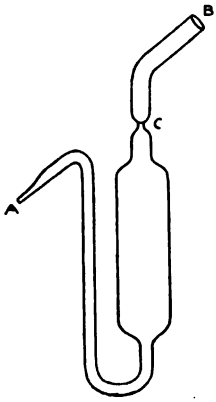

FIG. 116.

In this case the instrument (Fig. 116) is filled with the liquid in question and suspended by a wire inside a closed vessel containing the liquid, a thermometer, and an upright condenser.

The liquid is boiled and kept boiling for half an hour. Then, by means of a rubber tube slipped over *B* and a glass-rod pushed through it, the liquid is driven down *B* until the surface arrives exactly at point *C*, being driven over at *A*.

Having now the exact amount, draw back the rod to free the end *A*, close the ends, take out, dry, cool and weigh.

At high temperatures, the expansion of the vessel must be taken into consideration.

If the density be determined at $t'°$ C.,

Vol. of pyknometer at $t'° = V_t' = V_t\{1 + 0{\cdot}000025(t' - t)\}$

(where 0·000025 is the coefficient of cubical expansion of glass per degree C.)

$$= \frac{w_t}{d_t}(1 + 0{\cdot}000025(t' - t),$$

where w_t is the weight of water contained at $t°$, d_t the density of water at $t°$.

So we can get the density of the liquid at $t'° = \frac{w_{t'}}{v_{t'}}$, where $w_{t'}$ is the weight of the liquid at $t'°$ C.

Exercises.—1. Find the specific and molecular volumes of benzene, toluene and xylene at 25° C.

2. Find the specific volume of aniline at its boiling point.

Another method.—A pyknometer of capacity about 4 c.c. as used by Ramsay is shown in Fig. 117.

The interior volume is first determined by weighing full of air after cleaning with alcohol, heating and drying thoroughly, and then weighing full of air-free distilled water at ordinary temperatures.

The coefficient of expansion of glass may be determined by weighing full of water at 100° by the method described below.

Operations.—(1) Clean by washing with distilled alcohol, then evacuating with a vacuum pump.

(2) Fill with boiled distilled water by placing under water in a vacuum desiccator, reducing and increasing the pressure alternately. The last bubbles may be expelled by heating.

Then place the pyknometer in water for 20 minutes at a constant known temperature (a little above that of the balance case) and weigh.

Calculation.

Let w_1 be the weight of the pyknometer empty, w_2 weight filled with water at $t°$ C.

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Then internal volume at $t°$ C. $= V_t = \dfrac{w_2 - w_1 + \dfrac{w_2 - w_1}{d_t} \times 0{\cdot}001293}{d_t}$ to the first approximation.

Now fill with water at 100° by means of the apparatus shown in Fig. 118, which is heated by a small flame as it rests in a hole cut in a piece of asbestos mill-board. Raise or lower the instrument as necessary, and note the temperature of the steam and the pressure.

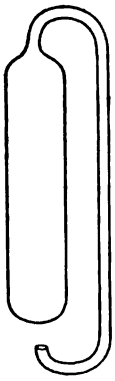

FIG. 117.

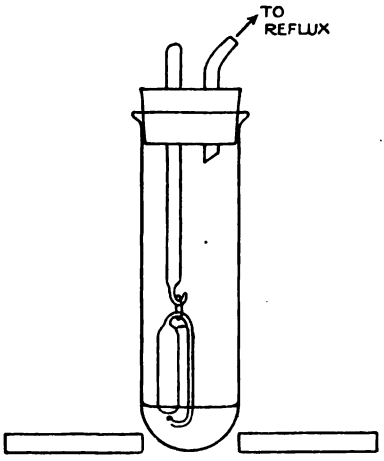

FIG. 118.

After heating in steam for 15-20 minutes, dry, hang in the balance case and weigh when cool.

Let w_3 be the weight of the pyknometer filled with water at the higher temperature T, D_T the water density.

Then internal volume at T

$$= v_T = \frac{w_3 - w_1}{D_T} + x,$$

allowing x for air displacement as before.

Hence, the mean coefficient of expansion is approximately

$$\frac{v_T - v_t}{(T - t)v_t},$$

where $t°$ is not high.

Empty with the aid of a vacuum desiccator, reclean and refill with another liquid, and so obtain the density of that liquid, operating as above.

Exercises.—By comparing the molecular volumes (at boiling point) of various bodies of definite differences in composition, it is possible to arrive at values for the atomic volumes of the elements in them. This has been done only for organic bodies (to any extent). Kopp, Thorpe, Lossen Schiff and

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Hortsmann have confirmed Kopp's conclusions generally. The atomic volume, however, is not strictly additive. See Nernst, *Theoretical Chemistry*, pp. 330 *ff*.

Suitable liquids to use for these exercises are:

For volume of CH_2 -	Ethyl formate and ethyl acetate.
,, ,, ,, $-O-$ -	A paraffin and an ether.
,, ,, ,, hydrogen	Butyl alcohol (Kopp).
,, ,, ,, carbon	Phenol.
,, ,, ,, O in OH -	Ethyl alcohol (compare with calculated volume).
,, ,, ,, Cl (etc.) -	Benzene and chloro (etc.) benzene.

The atomic volumes obtained by Kopp and others (though many authorities have disagreed) are:

C = 11.	Br = 27·8.
H = 5·5.	O(OH) = 7·8.
Cl = 22·8.	O(in CO) = 12·2.

Structure has a great effect on the volume.

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CHAPTER II.

SOLUBILITY.

1. **Gases in liquids.**—The *solubility* of a gas in a liquid is the volume of gas absorbed by 1 c.c. of the liquid under the conditions of the experiment.

The *absorption coefficient* is the volume of gas, reduced to 0° and 760 mm. pressure which would be absorbed in 1 c.c. of liquid if the pressure of gas above the liquid is 760 mm.

(*a*) **Direct method for gases not very soluble.**—The *solubility* and hence the *absorption coefficient* is easily found by a simple form of Heidenhaim and Meyer's apparatus, Fig. 119.

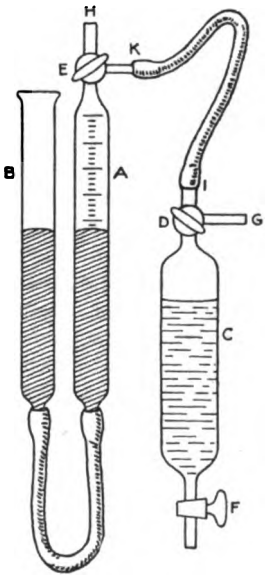

FIG. 119.

The determination is carried out thus:

A thermostat large enough to take the burette *B* and the pipette *C* employed to keep the temperature constant. The gas in the burette may be confined either over mercury, or, more accurately, over the solvent saturated with the gas in question, especially if the gas acts on mercury (*e.g.* chlorine).

The volume of *C* is found by filling it with water and allowing it to run into a graduated cylinder.

C is then filled with *air-free* distilled water, and both *C* and *B* placed in the thermostat. *A* is then filled to the tap *K* by connecting *A* and *H* and raising *B*. Connect *G* to the gas reservoir and pass a current of gas through *G*, *I*, *K*, *H*, to sweep air out of the connecting tube. Then lower *B* and by connecting *G*, *I*, *K*, *A*, draw a suitable volume of gas into *A*. Measure its volume at atmospheric pressure after leaving the apparatus for some minutes to assume the temperature of the bath. Now connect *A* with *C*, and by opening *F* and raising *B*, allow a definite volume of gas to enter *C*. Close *F* and measure this volume at atmospheric pressure. (The volume of water left in *C* is found by measuring the water run out.) Now close *D* and shake *C* thoroughly. Leave in the bath, connect *C* and *A*, and measure the gas left at atmospheric pressure. Repeat till no further absorption takes place.

Before taking each reading, allow the apparatus to stand in the thermostat for some minutes to attain a constant temperature.

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If V is the volume of liquid left in the pipette and v the volume of gas dissolved, then $\frac{v}{V}$ is the solubility under the conditions of the experiment.

If the atmospheric pressure be p, the temperature of the bath $T_1°$ absolute, and the vapour pressure of water at $T_1°$ be a, then the volume v, reduced to N.T.P., becomes

$$v \times \frac{273}{T_1} \times \frac{p-a}{760}.$$

Now if the pressure of the gas above the solvent had been 760 mm., then the volume absorbed would have been

$$v \times \frac{273}{T_1} \times \frac{p-a}{760} \times \frac{760}{p-a} = v \times \frac{273}{T_1}.$$

Hence the absorption coefficient is

$$\frac{v}{V} \times \frac{273}{T_1},$$

or

$$\text{Absorption coefficient} = \text{Solubility} \times \frac{273}{T_1}.$$

Suitable gases to use are CO_2 and N_2O.

(*b*) **Method for very soluble gases.**—Since the extremely soluble gases are all either acidic (HCl, etc., SO_2) or basic (NH_3) in character, the solubility is best found by saturating a small quantity of water with the gas. About 20 c.c. of water placed in a flask or wash-bottle is treated with a steady stream of the gas for 20 minutes. The gas is then stopped, the temperature allowed to become steady, the flask placed in a thermostat or water-bath, and the gas stream continued for another 10 minutes, using a delivery tube having a number of fine holes at the end dipping under the liquid. Finally the weight of gas dissolved is found volumetrically by diluting the liquid largely and titrating an aliquot part with a suitable reagent. The volume of gas dissolved is then found by calculation from its known density.

Exercises.—1. By the use of a mixture of CO_2 and N_2O of known composition, verify Dalton's law of partial pressures, after determining the solubilities of the two gases separately.

2. Distil (*a*) some concentrated hydrochloric acid (draught!); (*b*) some dilute hydrochloric acid, until in each case a constant boiling mixture is obtained. Note the boiling point of each and the barometric pressure. Titrate a measured volume of each with standard alkali. Conclusions?

Fit up an apparatus for varying the pressure under which distillation takes place, and repeat the above experiments at a different (but definite) pressure. Conclusions?

2. **Liquids in liquids.**—In binary liquid mixtures, the following cases arise:

(i) The liquids are insoluble in one another (mercury and water).

(ii) The liquids are completely miscible at all temperatures (alcohol and water).

(iii) The liquids are mutually soluble to a limited extent (ether and water).

In case (iii) the following variations arise:

(*a*) On *raising* the temperature, a point is reached at which the two liquids become completely miscible (phenol and water).

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(*b*) On *lowering* the temperature a point is reached at which the liquids becomecompletely miscible (triethylamine and water).

(*c*) On *either* raising *or* lowering the temperature, points are reached at which the liquids are completely miscible.

The solubility curves corresponding are shown in Figs. 120 A and B, and Fig. 121.

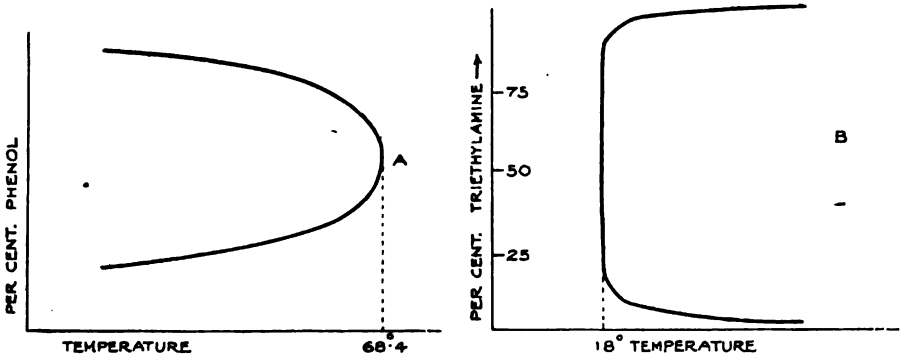

FIG. 120.

Fig. 120 A shows the solubility curve of phenol in water and water in phenol. The point *A* (called the critical solution temperature by Findlay, is the point at which complete miscibility first takes place (68·4° C., above which water and phenol are miscible in all proportions). Fig. 120 B shows a similar

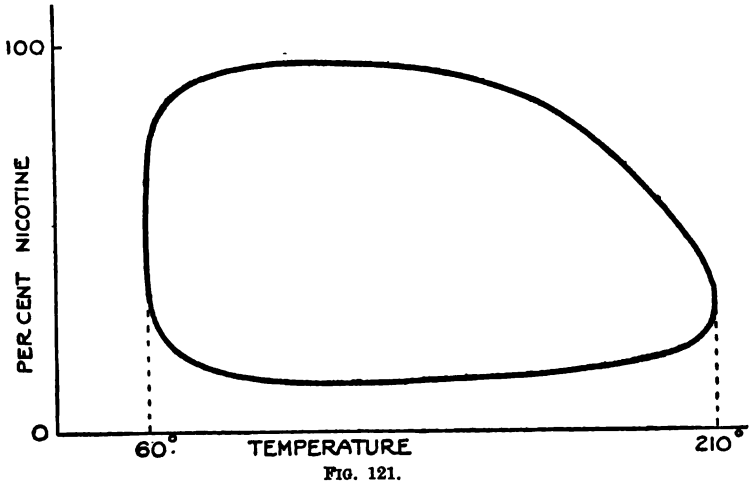

FIG. 121.

curve for triethylamine. In this case complete miscibility occurs *below* 18°. Fig. 121 shows the nicotine-water curve. Here complete miscibility is possible *above* 210° and *below* 60°.

Quantitative experiments on these mixtures are long and tedious, but the above phenomena may be studied qualitatively as follows :

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(*a*) *Phenol and water.*—Gradually warm a mixture of about equal volumes of phenol and water to about 70° C., with constant shaking. At some particular temperature the two layers will disappear. If the temperature is above 68·4°, addition of neither more phenol nor more water will cause the formation of two layers. On slowly cooling, separation into two layers will again take place. Allow the two layers to separate whilst the temperature is kept constant at, say, 40°. Then suddenly plunge the test-tube into cold water. Both layers become turbid owing to the decreased mutual solubility.

(*b*) *Triethylamine and water.*—These will be found to be completely miscible below 18°. On plunging the test-tube into hot water the mixture at once becomes turbid and separates into two layers.

(*c*) *Nicotine and water.*—See Hudson, *Z. Ph. Ch.*, 1904, **47**, 113. Also Flaschner, *Tr. Chem. Soc.*, 1909, **95**, 668; 1908, **93**, 1000. For a general discussion see Findlay, *The Phase Rule.*

Exercises. **Behaviour of mixed liquids on distillation.**—Distil mixtures of the following liquids, in each case using a thermometer and noting the variation or constancy of the boiling-points, and their relation to the boiling-points of the liquids.

(1) Benzene and water, or aniline and water (Regnault, *Pogg. Ann.*, **93**, 537).

(2) Isobutyl alcohol and water (Konowalow, *Wied. Ann.*, **14**, 34).

(3) Formic acid and water.

For full discussion of these see theoretical text-books.

3. **Solids in liquids.** (i) *Direct method.*—The saturated solution is prepared by shaking more than enough of the finely divided substance with the solvent in a thermostat at the required temperature for 3-4 hours. Alternatively, the substance may be warmed with the solvent with constant stirring to some 5-10° above that at which the determination is to be made, and then allowed to stand in the thermostat as before. When the solution is clear with deposited solid in the beaker, a portion is removed by means of a dry pipette (if the solution is above air temperature, warm the pipette before immersing it), transferred to a weighed weighing-bottle and weighed again. The solution is then transferred to a weighed evaporating basin, evaporated to dryness, and reheated if necessary until the weight is constant, care being taken that the temperature is sufficient to drive off the solvent but not to decompose the substance.

If the result has to be expressed in terms of grams per 100 c.c. of solution, the volume must be withdrawn accurately by a calibrated pipette.

(ii) *Indirect methods.*—If the body is fairly soluble and capable of direct volumetric or gravimetric analysis, these methods may be employed; *e.g.* in the case of chlorides, bromides, carbonates, oxalic acid, oxalates, ferrous salts, etc., etc. In general the solution is made up as above, and the portion used is diluted to a suitable strength for determination.

In the case of those bodies which are almost insoluble, special electrochemical methods may be employed (see p. 495).

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CHAPTER III.

DETERMINATION OF MOLECULAR WEIGHT OF GASES AND VAPOURS.

Methods.—(1) By direct measurement of density.
(2) By special methods.
(3) By vapour density determinations.
(*a*) Dumas' method.
(*b*) Victor Meyer's method.
(*c*) Hofmann's method.
(4) By determination of the "atomicity" of gases.

(1) **By direct measurement.**—The most accurate method consists of weighing the gas in a large bulb of measured volume.

A large bulb of some 200-300 c.c. capacity is blown and fitted with a wide capillary and tap, or alternatively a round-bottomed flask is taken and fitted with a well-fitting rubber stopper with a capillary tube and tap pushed through it.

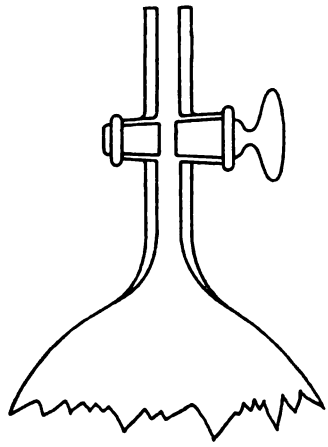

FIG. 122.

The first operation is to determine the volume of the bulb or flask.

Coat the tap with grease (2 parts vaseline and 1 part pure rubber melted together) and weigh the bulb empty after pumping out the air. Now open the tap carefully under distilled air-free water and let the bulb fill; close the tap and remove the water in the capillary above it by filter-paper.

Allow to come to a constant temperature and weigh to ·01 gram. The volume is then determined from the known density of water at the temperature of the determination, a correction being made for buoyancy of the air by counter-poising with a similar bulb.

The bulb is then emptied, washed with (*a*) alcohol, (*b*) ether, and exhausted twice to remove the ether vapour.

Now fill the bulb with the gas in question by connecting it to a Toepler (or other) pump barrel containing the gas, and forcing in the latter by raising the mercury reservoir.

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Let w_1 be the weight of the empty bulb, w_2 weight full of gas at $t°$, v_o volume of bulb at 0° C., and 760 mm., P the pressure.

Then $$v_o = \frac{v_t \times 273}{273+t} \times \frac{P}{760}.$$

And so the density referred to hydrogen is

$$\frac{w_2 - w_1}{v_o} \div \text{density of hydrogen.}$$

Allow for the expansion of the vessel—see previous experiments.

Exercise.—Determine the molecular weight of nitrogen peroxide at temperatures varying from 10° to 140° C. and plot a curve showing the dissociation of N_2O_4 into NO_2.

(If m is the degree of dissociation of N_2O_4, $1-m$ is undissociated, and $2m$ dissociated.)

$$\therefore \frac{D}{d} = \frac{1+m}{1}, \text{ etc.}$$

The student should work this out for himself.

(2) (*a*) **Determination by special methods.**—In many cases the density may be obtained by measuring the volume of gas evolved from a known weight of substance; or the gas, after being weighed, may be absorbed in a suitable liquid and this weighed, the specific gravity of the solution being noted.

Thus, the density of oxygen may be determined by observing the loss of weight on heating mercuric oxide, and at the same time measuring the volume of the gas evolved.

The density of CO_2 and SO_2 may be determined by weighing in a flask, absorbing in caustic potash and weighing same, allowing for the air in the bulb.

(*b*) **Modified method for the density of HCl, etc.**—Take a vessel as shown in Fig. 123, of about 50-75 c.c. capacity, also a supply of $\frac{N}{10}$ Na_2CO_3 solution.

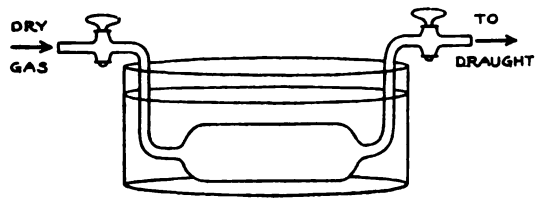

FIG. 123.

Fill the vessel as completely as possible by passing the gas for some time, and open under water.

The residual air is found by filling in the volume from a burette, while the weight of HCl is found by titration.

The volume of the vessel may be found by weighing with water as before, or roughly by means of a burette. Similarly determine the density of NH_3 and SO_2 by indirect titration.

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(3) **Molecular weight by vapour density methods.** (*a*) **Dumas' method.**—Take a bulb of about 100-200 c.c. capacity and of one of the shapes shown, weigh it full of air at a known temperature, and after warming it gently to expel some of the air, immerse the tip in the liquid.

After 10-15 c.c. of the latter are introduced, the whole is immersed in a constant temperature bath (preferably a boiling liquid) at a temperature of say 20°-30° C. above its boiling point. The tip should not be fouled by the vapour from the bath, and should therefore project slightly from the vessel. The liquid boils and vapour emerges quickly from the end.

If a flame be held near, it will be blown outwards, but care must be taken in the case of an inflammable liquid such as alcohol or ether not to bring the flame too close until the air has been expelled, or an explosion may result.

When the liquid has ceased to vaporise as shown by the cessation of the stream of vapour, the tip is sealed, the temperature of the bath and the pressure of the atmosphere noted, the flask is taken out, dried, cooled and weighed carefully, together with any glass taken off in sealing it.

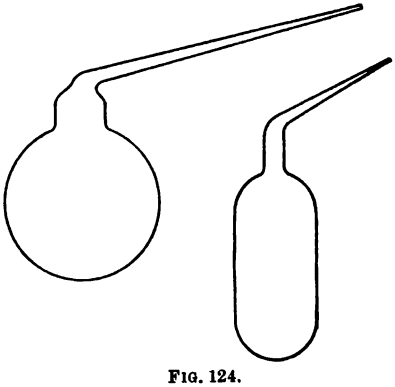

FIG. 124.

The tip is now broken off carefully under previously boiled air-free water, which rushes in and fills the vessel except for a small bubble which must be allowed for.

Note the temperature and weigh again with the broken tip.

Let the three weighings be w_1, w_2, and w_3 grams respectively, the pressure and temperature at sealing p and t, the temperature of water filling the bulb t'.

Then the volume of the bulb at $t'°$ is

$$(w_3 - w_1) \div \text{density of water at } t'° \text{ (see Tables).}$$

If an accurate result is needed a second approximation gives

$$\frac{w_3 - w_1}{d_{t'}}\left\{1 + \frac{1}{d_{t'}}\left(0{\cdot}001293 \times \frac{273}{273 + t'} \times \frac{p}{760}\right)\right\},$$

where 0·001293 gm. is the weight of 1 c.c. air at N.T.P.

Let this be $v_{t'}$.

Then $$v_t = v_{t'}\{1 + 0{\cdot}000025(t - t')\},$$

where 0·000025 is the coefficient of cub. expansion of glass.

The weight of vapour is

$$w_2 - w_1 + \text{weight of air contained at } t'°$$

$$= w_2 - w_1 + v_{t'}\left(0{\cdot}001293 \times \frac{273}{273 + t'} \times \frac{p}{760}\right).$$

Hence we know the volume at $t°$ and p mm. of the above weight of vapour. Reducing the volume v_t to that at 0° and 760 mm. we can calculate the density

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in grams per c.c. at N.T.P., supposing the vapour to have been capable of existence under those conditions.

To get the molecular weight, calculate the weight of 22,320 c.c. of vapour at N.T.P.

Thus find the molecular weight of alcohol or ether (water-bath); amyl alcohol (aniline-bath); liquids up to boiling point 150° (oil-bath).

(*b*) **Victor Meyer's method.**—Though this does not give the accuracy of Dumas' method, it is nevertheless so expeditious that it is generally employed, the determination being only required to verify which multiple of a determined empirical formula is the true molecular formula.

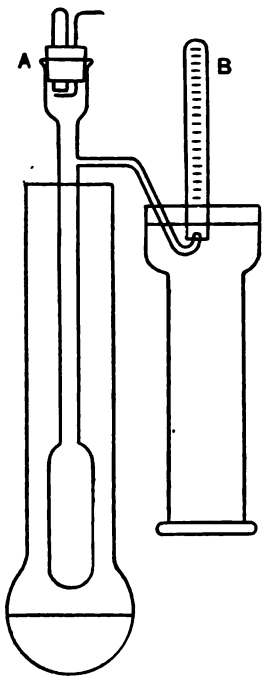

FIG. 125.

Principle.—A small weighed amount of a liquid is vaporised in an enclosure surrounded by a bath, displacing rapidly an equal volume of air which is collected and measured over water.

Precautions.—(1) The substance in the outer bath must have a sufficiently higher boiling-point than that of the liquid or vaporisation point of the solid under investigation to ensure that no time for convection currents is allowed before ebullition is complete, otherwise vapour will find its way over, condense and give too low a result.

(2) The inner vessel must be long, of ample volume, and heated for as much of its length as possible for the same reason.

(3) The liquid should be introduced by means of a small vessel in such a way that it is not vaporised before the final closing of the chamber, so that no disturbance of corks is necessary. This small vessel should be dropped, when everything is ready, by some device, a little mercury or asbestos being at the bottom of the chamber to prevent fracture of the latter. We may then assume that the displaced air has the same volume as the vapour would have had under the same conditions, for hot air was displaced by hot vapour.

Method.—The apparatus consists of a long tube of the shape shown, the bulb *A* at the bottom being about 200 c.c. in capacity. *A* is connected by means of a side tube with the graduated tube *B*.

At the bottom of *A* is placed a little asbestos (or mercury if the temperature of the bath is below 150° C.) to break the fall of the tube when it is allowed to fall in.

The external vessel holds a liquid of much higher boiling-point than the one the molecular weight of which is to be found, and is long in order to cover the inner vessel as far as possible. At the top of the inner vessel is an airtight rubber stopper with some device such as a rotating bent wire or side-tube with a sliding glass-rod to enable a small weighed stoppered tube or sealed bulb, containing about 0·1 gram of the liquid, to be held until all adjustments and temperatures are steady. (See Fig. 125.)

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Arrange the apparatus so that the side tube is under the water in the trough, but not under the measuring tube.

Heat the bath liquid to boiling and allow air to escape from the side tube; when no more bubbles emerge, drop the substance in *A* so that when at the bottom, the tube or bulb will open, the substance will vaporise and air will be displaced into the graduated tube.

Finally, transfer the graduated tube, keeping the end closed so that water cannot escape, to a deep cylinder containing water, depress till the levels inside and outside are the same, and read the volume, noting temperature and pressure. Reduce to N.T.P., allowing for the saturation pressure of water vapour.

$$\text{Volume at N.T.P.} = v \times \frac{273}{273+t} \times \frac{P-f}{760},$$

where f is the vapour pressure of water at $t°$ C.

Table of Vapour pressure of Water at different Temperatures (in millimetres).

Temp.	V.P.	Temp.	V.P.	Temp.	V.P.	Temp.	V.P.
0°	4·6	6°	7·0	12°	10·4	18°	15·3
1°	4·9	7°	7·5	13°	11·1	19°	16·3
2°	5·3	8°	8·0	14°	11 9	20°	17·4
3°	5·7	9°	8·5	15°	12·7	25°	23·5
4°	6·1	10°	9·1	16°	13·5	30°	31·5
5°	6·5	11°	9·8	17°	14·4	35°	41·8

By this means try chloroform, acetone, ether, methyl alcohol (water-bath);
liquids of b.p. 70°-90° (amyl alcohol or calcium chloride solution);
" " 90°-130° (aniline).

Either method may be adopted with suitable baths for the determination of the molecular weight of solids or liquids, thus obtaining the degree of association or dissociation.

In the case of association, if m is the molecular weight according to the expected formula, M that as found, then

$$\frac{M}{m} = x,$$

the association factor.

Examples.—1. Find the association factor of acetic acid at 120° C. and 180° C.

2. Find the dissociation factor of PCl_5 at various temperatures.

(*c*) **Hofmann's method.**—This consists of introducing a small quantity of a substance into a Torricellian vacuum at a temperature regulated by an external bath, the substance being weighed in a stoppered tube as in Victor Meyer's method. The temperature is maintained by means of the vapour of a boiling liquid a few degrees above the boiling-point of the substance in

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question under the conditions of the tube. The volume of the substance after the latter has been allowed to rise to the surface of the mercury in the tube, and there vaporise, is measured (the tube should be graduated and calibrated beforehand), also the height of the mercury.

The volume is determined, taking into account the expansion of the glass vessel if the temperature is high, and reduced to N.T.P by the expression

$$v_o = v_t \times \frac{273}{273+t} \times \frac{P-h-f}{760},$$

in which the student will easily recognise the terms.

Precautions.—1. To get any accuracy at all, it is essential that the substance be pure; a small amount of a volatile impurity will make a great difference to the result.

2. The stopper of the tube in which the substance is contained must be tied to the bottle neck by a short length of thread, otherwise it will, on reaching the vacuum, fly out with sufficient force to break the Hofmann tube.

(4) **Atomicity of gases.**—Once the atomic weight of a gas is known, the molecular weight is known if the number of atoms in the molecule has been determined.

The principle of the method is that if the ratio of the specific heats of a gas at constant pressure and constant volume be measured it should be $\gamma = \frac{5}{3}$. But in most cases the ratio is less than this owing to the fact that the molecules absorb internal energy, the ratio being $\frac{5+x}{3+x}$, where x is some positive quantity. The nearer the ratio is to unity, therefore, the more complex the molecule.

If $\gamma = 1{\cdot}66$, the gas molecule is monatomic,
1·4, ,, ,, diatomic,
1·33, ,, ,, triatomic,

and so on. (See tables in Physics books.)

There are three well-defined methods for finding γ:

(*a*) Direct determinations, Regnault's constant pressure, sp. ht.
Joly's constant volume, ,, ,,
and combination of the result. (See text-books of Physics.)

(*b*) Clement and Desormes' method.

(*c*) Kundt and Warburg's method / Resonance methods } and calculation of γ from the velocity of sound in the gas as given by these methods.

(*b*) **Clement and Desormes' method.**—If a gas expands or contracts adiabatically, *i.e.* with no gain or loss of heat from external sources, the pressures and volumes are related by the expression

$$p_1 v_1^{\gamma} = p_2 v_2^{\gamma},$$

where γ is the ratio of sp. hts.

Suppose the pressure of a large confined volume of gas to be increased suddenly from π (atmospheric) to p_1,

$$\pi v_o^{\gamma} = p_1 v_1^{\gamma},$$

where v_o and v_1 are the first and second volumes.

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After a time heat caused by the adiabatic compression will be conducted away, the temperature returning to the original value. The pressure falls to a new value, say p_2, such that $p_2 v_1 = \pi v_0$ if the volume has not been allowed to alter since the end of the adiabatic compression, the temperature being the same as it was originally.

$$\therefore \frac{v_1}{v_0} = \frac{\pi}{p_2} = \left(\frac{\pi}{p_1}\right)^{\frac{1}{\gamma}},$$

whence

$$\gamma = \frac{\log \pi - \log p_1}{\log \pi - \log p_2}.$$

Similarly the pressure may be suddenly diminished, etc.

Method.—Take a large glass flask, 20-30 cm. in diameter and fit it with a bung. Through the bung, bore holes to accommodate

(1) A wide tube *A* leading to a mercury reservoir by means of a flexible tube and clip.

(2) A manometer tube *B* fitted with a tap *D*.

(3) A narrow tube *C* fitted with a tap and leading to the outside air. (Fig. 126.)

The flask is placed in an enclosure and inverted, a support being placed below the bung to prevent accidents; mercury is now allowed to enter from the reservoir until it stands just in the neck of the flask as shown.

Through *C* introduce a thin layer of concentrated sulphuric acid to absorb all moisture as otherwise this will affect the result. The manometer tube should contain a non-volatile light liquid, *e.g.* some oil.

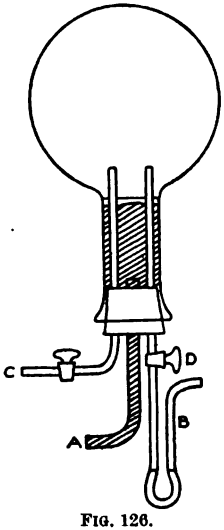

FIG. 126.

After setting up, open *C* to bring everything accurately to atmospheric pressure; close the clip on *A* after the temperature is constant. Raise the reservoir (*N.B.* A preliminary trial will show how far the reservoir must be raised to get a readable increase in pressure) and then suddenly open the clip. Close tap *D* and the clip when the pressure is a maximum and read off the increase of pressure carefully.

Now open *D* and when the pressure has again become constant read it.

Note.—1. If the differences of pressure are small, the differences of the logarithms may be taken as proportional to the differences of the pressures themselves.

2. An empty sulphuric acid carboy may be used for this experiment if a suitable bung can be obtained.

(*c*) **Kundt and Warburg's method.**—This depends on determining the velocity of sound in a gas from the wave length, and using the equation

$$v = \sqrt{\frac{\gamma p}{d}},$$

p and d being the pressure and density of the gas respectively under the conditions of the experiment.

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Kundt's tube is about 150-200 cm. long and of about 4 cm. diameter. Into it is fitted a glass-rod clamped at its mid-point and of about the same length as the tube. At the other end is placed a movable but well-fitting plunger covered with a layer of leather. Side tubes are provided near the ends for the introduction of the gas to be used.

Everything must be dried with care, lycopodium being then introduced as a thin layer along the bottom of the tube.

The rod AB is caused to vibrate longitudinally by stroking it with a rosined cloth or chamois leather; it is thus made to emit a high-pitched note. The piston D is now moved gradually inward until resonance takes place on stroking the rod, when the powder settles in little heaps along the tube. The piston A is then at a loop and D is at a node of the stationary vibration set-up.

The distances between consecutive loops, *i.e.* half a wave-length of the note, will be given by the distances between the ridges of powder (but take the reading over several ridges and divide by their number to get a more accurate result). Note the temperature.

Then $v = n\lambda$ where n is the frequency and λ the wave-length found.

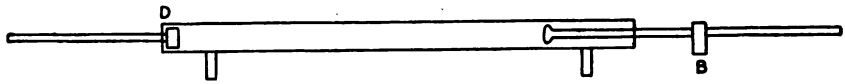

FIG. 127.

The frequency is found by comparing the length of wire in unison with the rod with that in unison with a standard fork, the frequencies of these two notes being inversely proportional to the respective lengths of wire.

If the velocity of sound in one gas is already known and that in another gas is desired, direct comparison may be made without determining the frequency of the rod.

If v_t and v_o are the velocities at $t°$ C. and 0° C. respectively,

$$v_t = \sqrt{\frac{\gamma p_o(1 + \alpha t)}{d_o}}$$

$$= v_o\left(1 + \frac{\alpha}{2}t\right) \text{ approximately,}$$

where α is the coefficient of increase of pressure of a gas at constant volume.

Finally v being known, γ can be found.

(*c* contd.) **Determination of the wave length by the resonance of a column of gas.**—This can be done with a fair degree of accuracy for heavy gases by means of a simple apparatus consisting of a glass-tube about one or two inches in diameter, and a wide cylinder such as that used in hydrometer determinations.

The tube is held in a clamp working on a vertical rack worked by a tangent hand-screw (Fig. 128).

The cylinder is partially filled with some suitable liquid (water, mercury, etc.).

Alternatively a tube connected by a flexible tube to a reservoir may be employed.

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The gas is delivered from a tube under the lower end of the resonance tube. A *slow* stream is kept up during the experiment.

A tuning-fork of known frequency (say 256) is struck, and the length of tube containing gas resounding to the fork is determined exactly.

The length of the tube in the first instance is $\frac{\lambda}{4} - x$, where x is a correction

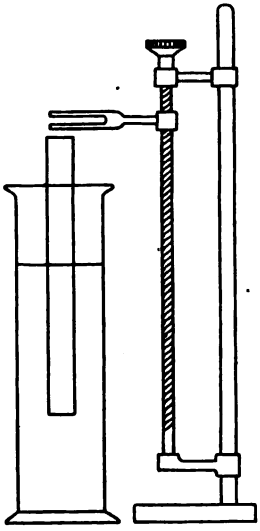

FIG. 128.

due to the non-coincidence of the end of the tube and the loop in the stationary vibration.

The tube is now lengthened until the next resonance occurs, the length then being $\frac{3\lambda}{4} - x$.

Hence $\frac{\lambda}{2}$ is read off by difference, and since $v = n\lambda$, v is thereby determined, hence γ as in the last experiment.

The student should devise any improvements and riders on this method.

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CHAPTER IV.

MOLECULAR WEIGHT DETERMINATION—LIQUIDS.

No methods for the accurate determination of the molecular weights of pure liquids are known. Several methods, however, are available which indicate the approximate molecular weight and give some idea as to the degree of association of the liquid molecules. These methods are indicated below.

1. **Trouton's law.**—If L is the latent heat of vaporisation of the liquid, and T the absolute temperature of the boiling-point at atmospheric pressure, then

$$\frac{ML}{T} = \text{a constant.}$$

The average value of this constant for normal liquids is 20·7 (Walden).

Hence

$$M = \frac{20{\cdot}7T}{L}.$$

For determination of latent heat of vaporisation see any book on Practical Physics. For boiling-point determination, see pp. 292 and 459 of this book.

The method is usually applied by assuming that the gaseous molecular weight, as found by density methods, is correct, and thus calculating the value of the constant. If this works out appreciably higher than 20·7, it is taken as indicating association in the liquid state.

2. **Surface tension methods** (Ramsay and Shields).—The forces acting on a molecule due to the attraction of other molecules are different at the surface of a liquid from that at any place within the liquid where the attraction can act in all directions. Hence there is a force acting inwards at right angles to the surface boundary, and the magnitude of this force per unit length of surface boundary is called the surface tension, γ.

As the surface is thus made to act as a stretched film, it possesses energy, and work is required to increase it. Hence the energy possessed by unit surface is the work required to increase it from zero to unity and is $\gamma \times 1 = \gamma$.

Surface tension is a colligative or molecular property, and by means of it molecular weights can be determined.

Several methods exist for the determination of surface tension; *e.g.*

(1) Capillary rise in a tube.
(2) Method of falling drops.
(3) Measurement of pressure inside a bubble.

Of these, the most universal and convenient is the first. (For details of the others see Poynting and Thomson's *Properties of Matter*.)

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When a capillary tube is immersed in a liquid, a column of liquid will be balanced in the tube above the exterior surface by the surface tension if the liquid wets the tube, the reverse occurring if the liquid does not wet the tube.

If the liquid makes an angle of contact θ with the walls of the vessel,

$$\gamma \cos \theta \times 2\pi r = \pi r^2 h\rho g + \pi r^3 - \tfrac{2}{3}\pi r^3$$

where r is the radius of the tube; h the rise or fall in the tube compared with the exterior surface; ρ the density of the liquid; g the acceleration due to gravity; γ being measured in dynes. (The last two terms of the equation give the correction for the volume of meniscus of liquid:—cylinder – hemisphere.)

So $$\gamma = \tfrac{1}{2}gr\rho \sec \theta\left(h + \frac{r}{3}\right).$$

If θ is zero, $\cos \theta = \sec \theta = 1$, this being the case when the liquid wets the tube.

Method.—Into a beaker, introduce some of the liquid, so that the latter stands about 2-3 inches high in the beaker. Fix a capillary tube of bore about 0·5 mm. in a clamp in such a way that it dips under the surface of the liquid. This capillary must be freed thoroughly from grease by continued washing in chromic acid mixture, then distilled water, finally redistilled alcohol cleared out with a current of clean air. On no account must the tube be touched near the ends with the fingers.

The capillary is now pressed up and down in the liquid to wet it thoroughly, and then it is raised from its lowest position. The whole is placed in a thermostat with transparent sides, after which the heights of the liquid surfaces in the boiling tube and the capillary are best determined by means of a travelling microscope with a vertical scale and a vernier, placed at a convenient distance from the beaker. The surface of liquid in the beaker is not easy to focus, and is usually found by a needle of accurately known length, the point of which is just touching the surface of the liquid. The microscope is then focussed on the top of the needle and on the surface of the liquid in the capillary. The height of liquid in the capillary is obviously this length plus the length of the needle.

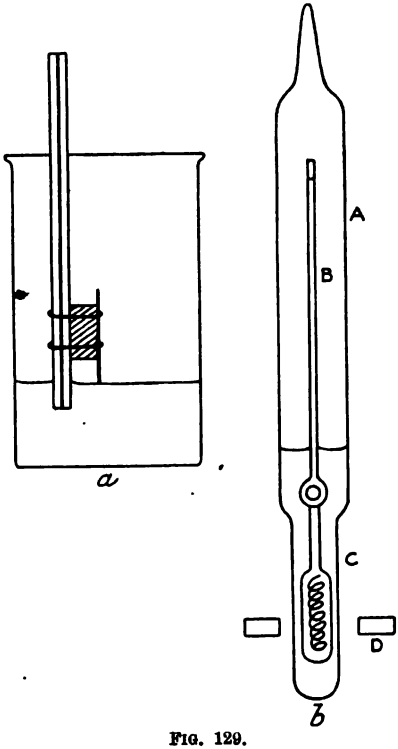

FIG. 129.

Note.—The needle must not be close to the capillary or to the side of the beaker for obvious reasons.

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If Ramsay and Shields' apparatus is available, it should be used. Fig. 129 *b* shows it in section. *A* is a tube containing the liquid (which has been boiled to expel air and the tube then sealed off), *B* is the capillary, *C* is a float containing a piece of iron wire, and *D* is a magnet by means of which the height of the capillary may be varied so that the liquid in it rises very nearly to the top. Finally, the radius of the capillary is measured by introducing a thread of pure mercury about 1·5 cms. long, the exact length of which is measured by the travelling microscope at various positions along the tube (which by this means should be proved to be uniform). This mercury is then expelled and weighed in a tared watch-glass. If $t°$ C. be the temperature at which the mercury was measured, then

$$\pi r^2 l \times \frac{13{\cdot}596}{1+0{\cdot}000181t} = w.$$

Hence r is found.

Determination of molecular weight or association factor.—Ramsay and Shields, using the method of Eötvös, calculate the molecular weight from the surface tension as follows (*Phil. Trans.*, 1893, **A. 184**, 647):

If γ be the surface tension per sq. cm., then γ multiplied by a suitable surface should vary as the temperature measured from the absolute zero for surface tension, *i.e. downwards* from the point at which $\gamma=0$. This temperature is, for most liquids, about 5° below the critical temperature. The suitable standard surface is the "molecular surface," *i.e.* the area of the face of the cube containing the gm. molecular volume. If v is the specific volume, then

$$\gamma(Mv)^{\frac{2}{3}} = \kappa\tau,$$

where M is the molecular weight.

τ is the "temperature" defined as above.

κ is a constant.

Taking measurements at two temperatures *at least* 10° apart.

$$\gamma_1(Mv_1)^{\frac{2}{3}} = \kappa\tau_1,$$
$$\gamma_2(Mv_2)^{\frac{2}{3}} = \kappa\tau_2.$$

And $\tau_1 - \tau_2 = t_2 - t_1$ (t = Centigrade temperature)

whence
$$\frac{\gamma_1(Mv_1)^{\frac{2}{3}} - \gamma_2(Mv_2)^{\frac{2}{3}}}{t_2 - t_1} = \kappa.$$

According to Ramsay and Shields' experiments $\kappa = 2{\cdot}12$ for most liquids.

Denoting the expression $\dfrac{\gamma_1 v_1^{\frac{2}{3}} - \gamma_2 v_2^{\frac{2}{3}}}{t_2 - t_1}$ by α,

then
$$M^{\frac{2}{3}}\alpha = 2{\cdot}12.$$

If instead of M we have to take xM to make this expression $= 2{\cdot}12$, then x is the "association factor."

Assuming M to be the molecular weight,

then $M^{\frac{2}{3}}\alpha = \kappa'$ (by experiment),

but $(xM)^{\frac{2}{3}}\alpha = 2{\cdot}12$,

whence
$$x^{\frac{2}{3}} = \frac{2{\cdot}12}{\kappa'}.$$

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1. Hence find the association factor of acetic acid at 40° and 80°, of water at 20° and 40°.

2. Find the molecular weight of benzene, ethyl acetate, etc.

3. **Walden's method** (*Z. Phys. Chem.*, 1909, **65**, 129, 257, 547).—Walden employs an expression which he calls the specific cohesion which is given thus :

$$a^2 = \frac{2\gamma}{\sigma},$$

where a is the specific cohesion, γ the surface tension, σ the density.

If both σ and γ are measured at the boiling-point (for which Ramsay's apparatus must be used) then Walden finds that

$$\frac{L}{a^2} = \text{a constant} = 17{\cdot}9$$

where L is the latent heat of vaporisation.

But according to Trouton's law,

$$\frac{ML}{T} = 20{\cdot}7.$$

Substituting the above value for L_1 we have

$$M = \frac{1{\cdot}16T}{a^2}.$$

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CHAPTER V.

MOLECULAR WEIGHT OF SUBSTANCES IN SOLUTION.

Molecular weights of substances in solution may be determined by

(1) Freezing-point determinations.
(2) Boiling-point determinations.
(3) Boiling-point modified and vapour pressure methods.
(4) Cooling curves.
(5) Osmotic pressure determinations.
(6) Partition coefficients and determination of association.

(1) **Freezing-point determinations.**—In very dilute solutions, the depression of the freezing-point of a solvent by equimolecular quantities of dissolved substances in the same volumes of solvents is, in normal circumstances, the same for different substances (non-electrolytes).

Hence, if K is the depression produced by m grams (the mol. wt.) in 100 grams of a given solvent,

then m grams in 100 gives depression K,

$$w \quad ,, \quad \text{in } W \quad ,, \quad \frac{Kw}{m} \times \frac{100}{W} = \text{(say) } d;$$

$$\therefore \; m = \frac{100wK}{Wd}.$$

If m is known, K can be calculated from the above expression. It is also found that

$$K = \frac{0{\cdot}02\,\tau^2}{L},$$

where τ is the freezing-point of the pure solvent and L its latent heat of fusion.

This method can be used only when there is no action of the solvent on the solute, or where they do not crystallise out together.

The following table gives the constants and latent heats for several solvents:

	K	L
Water	18·5°	79
Glacial acetic acid	38·9°	43
Benzene	49°	30·1
Naphthalene	70°	35·5
Nitro-benzene	71°	22·3

Beckmann's freezing-point apparatus.—This consists of a large vessel to act as cooling-bath, and in which a freezing mixture suited to the solvent can be placed. (Fig. 130 A.)

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In the cover placed on it are various holes *A* to take a wide boiling tube acting as an air jacket, and in which is corked the freezing-point tube-shaped as shewn, with a side tube to allow for the easy introduction of the substance. Another hole in the cover allows for the introduction of a stirrer.

The actual freezing-point tube is corked and a Beckmann thermometer (see below) and a stirrer are introduced through holes in the cork.

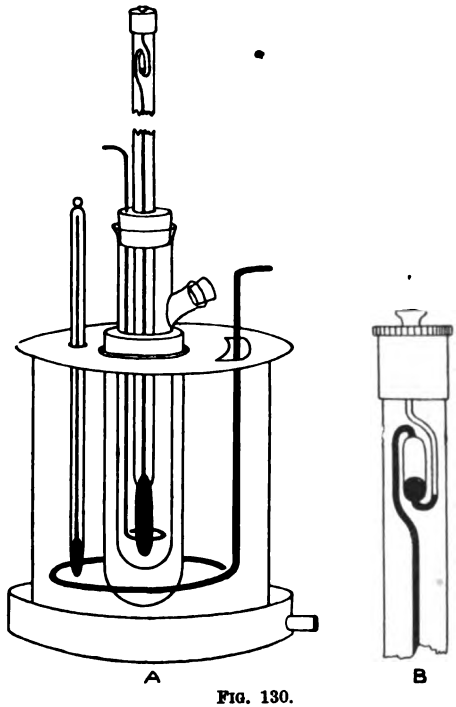

FIG. 130.

The thermometer (Fig. 130 B).—This is not constructed to read actual temperatures, as differences only are required, hence it has a range of 6° C. graduated in tenths and hundredths. There is a reservoir at the top, of the shape shown, to allow for adjustment to any desired range of temperatures.

Suppose when adjustment is required that there is too much mercury in the bulb at the bottom at first. Expand the mercury by warming to some 4°-5° higher than the temperature of the freezing solvent, so that the mercury will extend into the upper reservoir and form a globule at the top. This can be shaken off by tapping smartly against the hand. On cooling, the mercury thread should stand somewhere between the top (5th to 6th) two degrees. If not, the thread must be readjusted, and this may be done by noticing the rate at which it rises, calculating the right moment to detach the thread.

Note.—A separate thermometer should be used for boiling-point determinations owing to the difficulty of glass bulbs not settling down to correct volumes with ease after warming.

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Points to be noted when making determinations are:

(1) Do not make the temperature of the cooling-bath more than a few degrees below the freezing-point of the solvent, otherwise the temperature found will be a compromise between the rate of cooling of the solution and its freezing-point. Furthermore the concentration may be altered owing to the rapid solidification of the solvent.

(2) Avoid super-cooling to more than half a degree, or even less. This may be attained by stirring very vigorously or by the introduction of a very small portion of the pure solid solvent, taking care that the amount added is so small that it cannot affect appreciably the concentration of the solution.

(3) Many readings must be taken in order to give as good a result as possible, not differing by more than 0·002°, and the thermometer should be tapped when a reading is desired.

The procedure is illustrated by a specific case.

Determination of the M.W. of camphor in benzene.—First set up the apparatus, and from a stoppered or corked weighing tube, pour out some 20 gm. pure benzene, weighing accurately by difference.

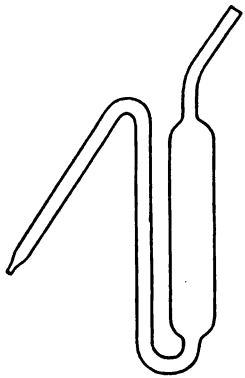

FIG. 131.

The thermometer having been set previously so that in freezing benzene (5·5° C.) the thread stands in the top degree of the scale, it is placed so that the bulb is completely immersed in the benzene in the tube.

The outer bath should have ice or iced water kept at about 2-3° C. by regulating the addition of ice.

The freezing-point of benzene is then determined accurately. Do not let more than 0·3° C. of super-cooling take place, but stir vigorously. When the thermometer thread begins to rise, stir slowly and note the maximum temperature attained.

Take out the tube, melt with the hand, and re-determine at least twice.

Next, a small weighed portion (0·1-0·2 gm.) of the substance is introduced in the form of a tablet or compressed rod through the side tube; if a liquid solute, it is introduced from a pipette with a long tube (Fig. 131).

The freezing-point is more difficult to determine than that of the pure solvent, so that at least four more determinations will be required. The same precautions re super-cooling and stirring must be adopted.

Repeat by adding further small portions until altogether about 0·6-0·8 gms. of substance have been added.

Thus try benzoic acid or anthracene in benzene; sodium chloride or sulphate in water.

In the latter cases, note that an abnormal depression will occur. This is due to dissociation if the depression is great, to association if apparently too small.

Thus, supposing x to be the "degree of association," then $1-x+\frac{x}{n}$ as

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compared with 1 will be the number of particles, if n molecules associate to form one "entity."

So
$$\frac{d_{\text{calculated}}}{d_{\text{found}}} = \frac{1}{1 - x + \frac{x}{n}}.$$

$$x = \frac{d_{\text{calc.}} - d_{\text{found}}}{d_{\text{calc}}\left(1 - \frac{1}{n}\right)},$$

or in the case of dissociation

$$\frac{d_{\text{ alc.}}}{d_{\text{found}}} = \frac{1}{1 - x + nx}, \text{ etc.}$$

Hence find the degree of dissociation of acetic acid in water, etc., and confirm by boiling-point determinations (see below).

For benzoic acid in benzene $n = 2$ (association).
,, acetic acid in water $n = 2$ (dissociation).
,, sodium chloride in water $n = 2$ (,,).

(2) **Elevation of the boiling-point** (*Beckmann's method*).—The principle is precisely the same as that of finding the depression of the freezing-point of a solution. (L, of course = latent heat of vaporisation.)

The constants are, of course, different, and a table is here given of constants for the chief solvents.

	K.	L.
Benzene	26·7°	96·2
Ethyl alcohol	11·5°	215
,, ether	21·2°	87·4.
Acetone	16·7°	125.
Water	5·2°	540.

Beckmann's apparatus.—The boiling-point tube consists of a fairly narrow tube A of the shape shown with two side tubes, one of which contains a small condenser B. (Fig. 132.)

A small ring burner should be used, and above it is placed a wire gauze coated, except for a small ring C in the centre, with a sheet of asbestos D.

A short glass cylinder E with a mica plate F is fixed up, and the tube let down through the hole in F until it is nearly touching C; it is then clamped in position.

The thermometer is similar to that described in the last experiment; it is set so that the mercury thread stands in the bottom degree when the bulb is immersed in the pure boiling solvent.

Before fixing the thermometer, the tube A is filled to one-third of its height with glass beads or platinum tetrahedra, a platinum wire being often sealed through the bottom in order to secure regular ebullition without superheating or bumping.

The thermometer bulb extends to within a few millimetres of the beads when all is fixed; then, about 20 gms. of solvent are introduced through the side tube from a corked tube, by difference.

After the apparatus is corked, the boiling-point of the solvent is found, care being taken to keep the boiling steady, as otherwise the mercury thread

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will keep on going up and down. Draughts must be avoided, and the flame screened from such as there are. It is advisable at times to place the flame slightly to the side of the hole in the asbestos, not directly underneath the boiling tube.

When the thermometer has become stationary for 15-20 minutes, note the reading and let all cool.

Meanwhile small tablets of the substance of about 0·1 to 0·2 gm. are compressed in a compressing apparatus (one may be improvised by two glass rods in each end of a glass tube) and weighed. These tablets may be introduced easily through the side tube.

The solution is then re-heated and the boiling-point noted when it has been constant for 5-10 minutes. More substance is then introduced, and the operations repeated at least three times.

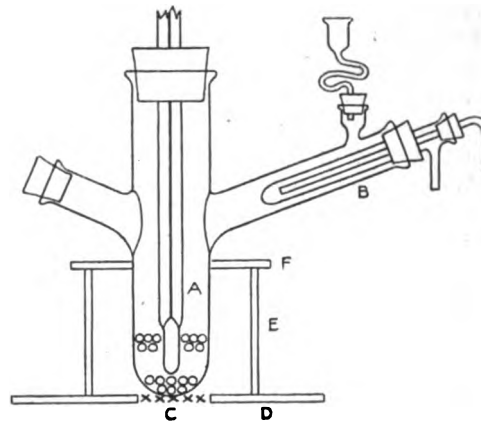

FIG. 132.

The same formulae hold good as for freezing-point determinations. A correction for the weight of the vapour in the tube and condenser is needed for accuracy.

Hence, using benzene as a solvent, find the m.wts. of benzoic acid, phenol or camphor. Acetone is a useful solvent also for a number of compounds.

(3) **Elevation of the boiling-point (modified).** (*a*) **Walker-Lumsden method of using Landsberger's apparatus** (*J.C.S.*, 1898).—In this case the latent heat of vaporisation of a solvent is utilised for heating the solution, and although the boiling-point of the solution will be above the temperature of the vapour, yet the determination is possible on account of the magnitude of the latent heat. A liquid of high latent heat is therefore required, also the molecular elevation must be great to enable speed to be combined with accuracy. Alcohol and ether are suitable solvents, but benzene has a low latent heat and water a low molecular elevation.

In this experiment we employ an amount of a substance in a measured *volume*, not weight, of solution.

If K is the molecular constant, w the weight of the substance in grams,

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and v the volume of the solution in c.cs., d being the increase in boiling-point,

$$M = \frac{Kw}{dv}.$$

Walker-Lumsden constants for a few liquids are as follows:

	K.*	B.Pt.
Alcohol	1560	78° C.
Ether	3030	35° C.
Benzene	3280	80° C.
Acetone	2220	56° C.
Water	540	100° C.
Chloroform	2600	61° C.

* K = rise of b.pt. for 1 gm.-mol. in 1 c.c. of solution.

Apparatus.—A convenient form may be made as follows:

Blow a tube *A* of the shape shown with a side tube which reaches well up the side. The diameter of the tube should be 2-3 cm., and that of the side tube say 5 mm. The tube should be about 12-15 cm. long, and the side tube 7-8 cm. The thermometer to be used, reading to 0·05° C., should be graduated carefully and fixed in position a constant distance through the cork.

The tube, after coating with a thin layer of paraffin wax, is clamped lightly along a grooved board. Then, by means of a long lever with two points, a millimetre scale is scratched out along the greater part of the tube, after which the paraffin wax with marks is painted over with hydrofluoric acid solution for 5 minutes. Finally wash well off, and the tube is ready for calibration. Fix the cork with thermometer in position, and either small platinum tetrahedra, glass beads or nickel gauze at the junction inside the tube to break vapour into small bubbles as it enters the tube.

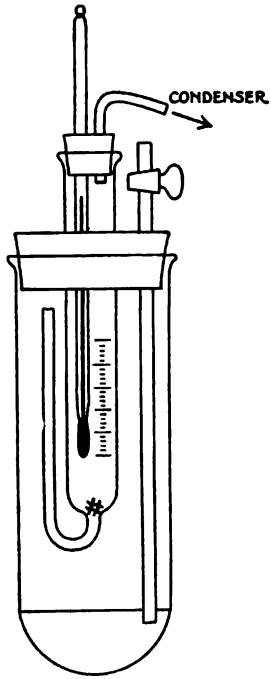

FIG. 133.

With all these in position, calibrate the tube by running in water from a burette through the side tube, noting the volume carefully as it rises to the various millimetre marks. Then draw a calibration curve (volumes against readings on the scale).

Fix the boiling-point tube into a large boiling-tube by means of a cork, and provide a glass tube as shown as a safety valve. This can be provided with a screw clip to allow for an adjustment of pressure when necessary.

Firstly, to find the boiling-point of the solvent, put more than enough to cover the bulb of the thermometer in the graduated tube, and some pieces of capillary tubes with a suitable amount of the solvent in the outer (boiling) tube.

Warm the outer tube carefully, and by boiling the solvent in the boiling

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tube allow vapour to pass into the graduated tube through the side tube until the thermometer is constant.

Secondly, introduce 0·5 to 1 gram of the substance, after weighing carefully, into the graduated tube, and after reheating and passing the vapour through the solution for some minutes, take the temperature and note the volume, the latter being known from the calibration curve.

The temperature, will, of course, vary as the dilution increases, but this will not affect the accuracy of the result.

Repeat twice more, and make the necessary calculations. Several modifications of the above experiment have been suggested. See Walker and Lumsden, *J.C.S.*, 1898; Ludlam, *J.C.S.*, 1902, p. 1194.

Thus try camphor in benzene; urea in alcohol; benzamide in water (association); benzoic acid or aniline in ether (special precautions for safety); salts in water (dissociation).

3 (*b*) **Vapour tension methods.**—There are two or three ways of determining molecular weight by vapour tension methods, one of which by Ostwald, and by Will and Bredig, depends on the aspiration of dry air, through first the solution and then the solvent in succession in one experiment.

The loss of weight of the solution is proportional to the vapour tension of the solution.

The loss of weight of the solvent to the difference between the v.t. of solvent and solution.

Hence
$$\frac{p'}{p-p'}=\frac{\text{loss of solution}}{\text{loss of solvent}}=\frac{m}{M}\cdot\frac{w}{W}.$$

where w grams of substance are dissolved in W gms. of solution, m and M being the molecular weights of the solute and solvent respectively.

The dilute solution and solvent may be contained in successive potash bulbs whilst dry air at the rate of two bubbles per second may be aspirated through, the apparatus being placed in a thermostat.

Try benzoic acid in ether (for precautions with ether vapour see Organic Preparations, pp. 284 and 302).

3 (*c*) **Blackman's method.**—In solutions having the same vapour pressure, concentrations are such that the volumes are inversely proportional to the molecular weights of the solutes.

Boil solutions of two substances in the same solvent, *e.g.* ether, in tubes as shown in Fig. 134, which have been calibrated as for the Walker-Lumsden apparatus, and carry on for about 90 minutes, condensing the vapour until the volumes remain constant for some time. The usual precautions against "bumping" are necessary.

If the mol.-wt. of one substance be known, then that of the other follows by comparison.

4. **Cooling curve methods. Depression of melting-point.**—The theory of this method is exactly the same as in the case of freezing-point determinations.

By determining the rate of cooling of a solution of a substance in a solvent which is solid at ordinary temperatures, we can determine the depression of the m.pt.

Determination of the molecular weight of *o*-nitro-phenol in naphthalene or *a*-naphthol in azo-benzene.

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Set up a test-tube fixed into a boiling-tube by means of a cork, the space between the tubes acting as a cushion, giving more uniform cooling.

The boiling-tube is immersed in a constant temperature enclosure or bath of suitable temperature, whilst the test-tube contains a thermometer reading to at least tenths of degrees.

The inner tube, containing about 12-15 grams of naphthalene weighed exactly, is warmed until the latter has melted and the temperature has risen some 10°-15° above the melting-point.

It is then set up and allowed to cool, the temperature being taken every half or quarter-minute.

At the melting-point, the temperature will remain stationary for a long time whilst the latent heat is being evolved.

From the readings, draw a curve of temperature and time. (Care must be taken that the thermometer bulb is completely immersed in the melted naphthalene and that the thread is visible in the neighbourhood of 75°-80° C.)

o-nitrophenol is then added in instalments of about 0·5-1 gram at a time until three different amounts have been added, the melting-point being redetermined each time.

If Δ is the molecular depression, w the weight of naphthalene, W the weight of solvent, then $M = \frac{100w\Delta}{Wd}$.

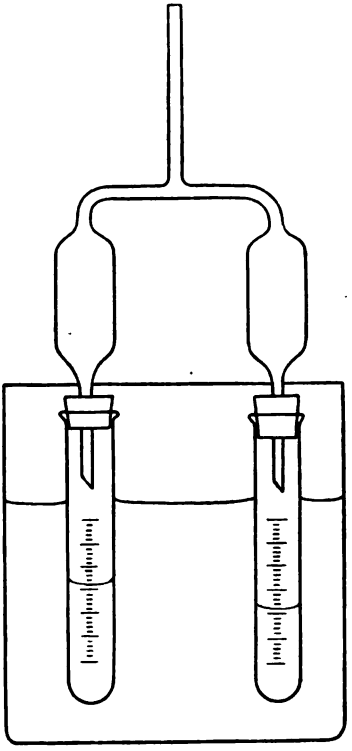

FIG. 134.

Table of Molecular lowering of Melting-points of solvents.

Solvent.	M.P.	Δ	Latent ht. of fusion.
Diphenyl - - -	70°·2	82	28·5
Diphenylamine - -	54°	88	24
Azo-benzene - -	66°	82	27·9
p-Toluidine - -	42·5°	52	39
Naphthalene - -	80°	71	35·5
Naphthylamine - -	50·1°	78	25·6
Stearic acid - -	64°	44	47·6
Phenol - - -	39°	74	25

5. **Osmotic pressure methods.**—Direct measurement of osmotic pressure is a very tedious and difficult operation, and the student is here simply referred to original papers: Morse and Horne, *Am. Ch. J.*, 1901, p. 80; Berkeley and Hartley, *Phil. Trans.*, **206**, 481 (1906).

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It may be noted that the osmotic pressure of a solution may be found approximately from its freezing-point, for it is found by experiment that a normal solution of a non-electrolyte in water freezes at $-1°{\cdot}86$ and has an osmotic pressure of 22 atm. Hence the O.P. of any aqueous solution is obtained from the lowering of the freezing-point (J) by the relation

$$\delta \times \frac{22}{1{\cdot}86} = \text{O.P. (in atmospheres)}.$$

6. **Partition coefficients. Distribution of substances between solvents.**—There is always a definite ratio according to which a substance will divide itself between two solvents which are non-miscible or only partially miscible. This is of great importance in the extraction of organic substances by ether.

The ratio $K = \frac{c_1}{c_2}$, where c_1 and c_2 are the concentrations in the two solvents, is called the *Partition coefficient.*

If, however, the substance is associated or dissociated in either solvent, this no longer holds good.

Suppose n molecules associate into one

$$nM = M_n$$

where M and M_n are the molecular weights of single and associated molecules respectively.

By the law of mass action

$$C_M^n = kC_{Mn}, \quad \text{or} \quad C_M \propto \sqrt[n]{C_{Mn}}.$$

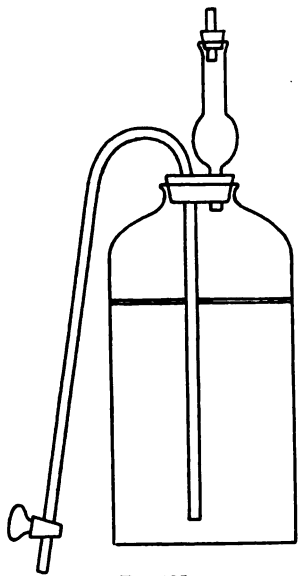

FIG. 135.

The constant now becomes the ratio between the concentrations of "single molecules" in the two solvents or

$$K = \frac{\sqrt[m]{c_1}}{\sqrt[n]{c_2}},$$

where m and n are the associations respectively.

So relative molecular weights may be determined.

The Method in principle consists in shaking a solution of the substance in one of the solvents with the other solvent for some time in a thermostat and then withdrawing a portion of each layer in order to determine by suitable chemical or physical means the amount of substance therein.

If an organic acid is the subject of the experiment a titration is performed by means of $\frac{N}{20}$ or $\frac{N}{40}$ baryta solution, using phenolphthalein as an indicator.

For this purpose prepare

(*a*) Carbonic acid-free water.

(*b*) Standard baryta water (see volumetric analysis).

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(*a*) Water is freed from CO_2 by boiling it and drawing through it a current of pure outdoor air which has been passed through a soda-lime tube and a layer of glass-wool to arrest dust.

The water must be kept in a reservoir under a layer of paraffin and syphoned off from a clipped tube. The inlet for air to the reservoir should be protected by a soda-lime tube. (Fig. 135.)

This CO_2-free water must be used in making up the solutions of organic acids and of baryta.

Determination of the coefficient of distribution of succinic acid between ether and water.—In a stoppered vessel place 100 c.c. of a 0·3 to 1 per cent. succinic acid solution and add an equal volume of ether. Place the vessel in a thermostat at, say 25° C., and shake frequently and thoroughly during the course of half an hour. Finally, after shaking round and round to loosen any drops adhering to the sides and allowing the layers to separate, syphon off 10 or more c.cs. of each solution and titrate with $\frac{N}{20}$ baryta water. Carry out repeated extractions by adding water each time and analysing all extractions.

Determine c_1, c_2, $\frac{c_1}{c_2}$.

Similarly find the coefficients in the case of

$$\left.\begin{array}{l}\text{Tartaric acid}\\ \text{Benzoic acid}\\ \text{Salicylic acid}\end{array}\right\}\begin{array}{l}\text{between benzene and water}\\ \text{or chloroform and water,}\end{array}$$

and calculate c_1, c_2, $\frac{c_1}{c_2}$, $\frac{c_1}{\sqrt{c_2}}$, where c_2 is the concentration in chloroform or benzene; hence prove whether the acids are associated at different concentrations, and if so, find the law according to which this occurs. (See Nernst, *J.C.S.* abstracts, 1891, p. 1148.)

Also find the coefficient for iodine between carbon disulphide and water at 15° C. (ratio = 410). (Titrate the aqueous extract with $\frac{N}{100}$ thiosulphate.)

Determination of the degree of dissociation of bimolecular salicylic acid in benzene from a knowledge of the partition laws.—On dilution, the bimolecular molecules dissociate into single ones, and the single ones in water into ions (slightly).

Hence, it should be possible to determine the degree of the latter from the change in value of $\frac{c_1}{\sqrt{c_2}}$.

Let c_1 be the concn. in water, c_2 be the concn. in benzene of the double molecules, α the degree of ionisation in water, K the affinity constant of the acid.

From Oswald's dilution law:

$$K = \frac{\alpha^2}{(1-\alpha)v}$$

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where v is the dilution (*i.e.* volume (in litres) containing the gram mol.-wt. of acid), or

$$\alpha^2 + \alpha K v - v K = 0;$$

$$\therefore \ \alpha = \frac{Kv}{2}\left(\sqrt{1+\frac{4}{Kv}}-1\right)$$

Hence α is known.

For salicylic acid, $K = 1{\cdot}02 \times 10^{-3}$.
,, acetic ,, $K = 1{\cdot}8 \times 10^{-5}$.
,, benzoic ,, $K = 6 \times 10^{-5}$.

But if k is the ratio of the concentrations of single molecules in water and benzene, then it must equal $\dfrac{c_1(1-\alpha)}{m}$

where m is the concentration of single molecules in benzene,

$$(1) \ \therefore \ m = \frac{c_1(1-\alpha)}{k}.$$

Now the concentration of double molecules is $c_2 - m$,

$$(2) \ \therefore \ \frac{m^2}{c_2 - m} = c_1,$$

a constant, from the law of mass action, this constant being the dissociation constant of complex molecules.

Substituting in (2) the value of m given in (1), we have

$$\frac{c_1^2(1-\alpha)^2}{k^2c^2 - c_1k(1-\alpha)} = C = \frac{c'^2_1(1-\alpha')^2}{k^2c'_2 - c'_1k(1-\alpha')}$$

if c'_1 and c'_2 refer to corresponding values at another dilution (for C and k are independent of dilution).

Here k is the only unknown, so it can be found, hence also m and C.

The experiment is carried out as for succinic acid, ether and water, using about 5, 2·5 and 1 gram of acid respectively in 200 c.c. each of benzene and water. Titrate portions of the aqueous solutions with $\frac{N}{50}$ baryta water, and hence deduce the concentrations in the benzene solution.

Determination of the degree of hydrolysis of aniline hydrochloride in water at 25° C.—The partition coefficient of aniline is first determined by shaking in the usual way 500 c.c. water and 75 c.c. benzene with 5-10 grams aniline. The aniline in the benzene layer is determined by titration with bromine water of known titre. (See Book V. for details, p. 423.) The titration should be carried out in a stoppered bottle with thorough shaking. (Employ a small aliquot part of the benzene layer.)

Then, a known amount of aniline hydrochloride is dissolved in 1000 c.c. water, 75 c.c. of benzene added, shaken, and again the amount of aniline in the benzene solution is determined. The theory is as follows:

When a salt of a weak base or weak acid is dissolved in water, hydrolysis takes place according to the equation

$$\text{salt} + \text{water} \rightleftharpoons \text{acid} + \text{base},$$

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and the equilibrium is defined by the law of mass action,

$$c_1c_2 = kc_3c_4,$$

where c_1, c_2, etc., are the respective molecular concentrations.

This can be studied by determining the partition of the base or acid between water and another solvent, *e.g.* benzene.

Let a be the initial amount of HCl in gm. equivalents; b be the initial amount of aniline in gm. equivalents; k be the partition coefficient of aniline between water and benzene; v the volume of benzene per litre of water.

At equilibrium, c_4 is the concentration in gram equivalents per litre, of aniline in the water layer.

$$\therefore\ c_4kv \text{ is that in benzene.}$$

As the total amount of free base is then $c_4(1+kv)$ and the initial amount was b, then

$$b - c_4(1+kv)$$

must still be left as salt and it is in the aqueous layer $= c_1$.

The amount of acid originally was a, hence the rest of the acid not in the salt must be

$$a - b + c_4(1+kv) = c_3.$$

Substituting in the first mass action equation

$$b - c_4(1+kv) = \frac{k}{c_2}(a - b + c_4(1+kv))c_4.$$

Now $\frac{k}{c_2}$ is constant because c_2 is constant. Let it equal C.

As the salt had been taken dissolved in water, the acid and base are in equivalent proportions,

$$\therefore\ c_3 = c_4, \text{ and } c_1 = b - c_4.$$

$$\therefore\ b - c_4 = Cc_4^2.$$

Since C has been determined and b is known, c_4 is calculated.

The degree of hydrolysis is the ratio of free base in water actually present compared with the whole of the base used as salt, *i.e.* $\frac{c_4}{b}$, or 100 times this if expressed as a percentage.

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CHAPTER VI.

ADDITIVE PROPERTIES OF THE MOLECULE.

1. MOLECULAR VOLUMES—already dealt with.
2. REFRACTIVITY.

3. **Refractivity. Use of the Pulfrich refractometer.**—When a ray of light passes from one medium to another obliquely, it suffers refraction according to the law

$$\frac{n}{N} = \frac{\sin i}{\sin r},$$

N and n being the refractive indices of the second and first medium respectively, i and r the angles of incidence and refraction.

When travelling from a dense to a lighter medium, if the incidence is greater than a certain angle called the critical angle, the ray cannot pass

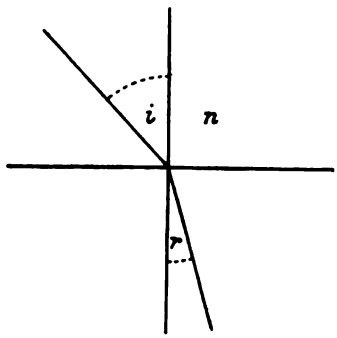

FIG. 136.

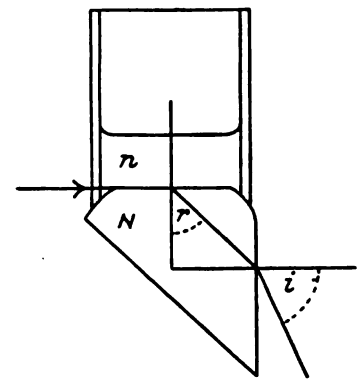

FIG. 137.

through the surface, but is totally reflected at the critical angle when the angle of refraction is 90°,

$$\frac{\sin 90°}{\sin r} = \frac{N}{n} \qquad r = \sin^{-1}\frac{n}{N}.$$

The principle of *Pulfrich refractometer* lies in the use of a dense right-angled prism of glass with bevelled edges on the top surface, and to which is cemented a cell containing liquid the lower side of which is transparent. A diagrammatic section is shown in Fig. 137.

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Let N be the R.I. of the glass, n that of the liquid standing in the cell.

Then
$$\frac{n}{N} = \sin r$$
if the light ray approaches along the surface liquid-glass, n being smaller than N.

At the second surface, taking air as having a R.I. of unity,
$$N = \frac{\sin i}{\sin(90^\circ - r)} = \frac{\sin i}{\cos r}.$$
$$\therefore\ N^2 \cos^2 r = \sin^2 i$$
$$N^2(1 - \sin^2 r) = N^2\left(1 - \frac{n^2}{N^2}\right) = \sin^2 i.$$
whence
$$n = \sqrt{N^2 - \sin^2 i}.$$
If we measure i, the angle at which the light emerges from the prism, n can be found.

Gladstone and *Dale* found that $\frac{n-1}{d}$, where d is the density, is nearly constant for substances at various temperatures, while *Lorentz* and *Lorenz* independently deduced that the formula
$$\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$$
is a constant depending only on the nature of the substance.

This expression is termed the specific refractivity of the substance, the molecular refractivity being
$$\frac{M}{d} \cdot \frac{n^2-1}{n^2+2}.$$
The latter expresses an " additive " property of the substance.

To perform the experiment, it is necessary to use monochromatic light. This may be obtained by means of a sodium flame or from the spectrum lines of rarefied gases with the aid of an induction coil.

The *sodium flame* may be obtained by heating a salt of sodium on a ring of asbestos bound on to the tip of a bunsen burner or on a loop of platinum wire or gauze. A protecting circular wall having a small hole on one side protects the flame from draughts.

The C and F lines of the hydrogen spectrum may be used, being produced conveniently in a Geissler tube of the shape shown in order to allow for its use in the end-on position when a greater illumination will be brought to bear. (Fig. 138.)

Regulation of temperature.—As temperature changes make a great difference, not only in the R.I. of the solution, but also of the glass, a constant temperature is maintained by currents of water circulated as shown in the figure. (Fig. 139.)

The prism is surrounded by a metal box A, through which the water circulates. The water is then led into the box B, which is immersed right into the liquid and serves to cool or warm the latter. The thermometer inserted in position indicates the temperature of the liquid on the prism.

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The Pulfrich refractometer is shown in Fig. 140, the heating (or cooling) apparatus being shown separately in Fig. 139 to avoid confusion.

A prism *P* carries on its upper face the glass cell *C*, in which is placed the liquid under experiment. The prism is surrounded on all sides except that nearest the telescope *T* by a metal box through which water circulates as already described. *D* is a graduated circle with a vernier (not shown), *E* is the eye-piece, *S* is a slow motion screw, and *K* is a clamping screw which brings the slow motion into action.

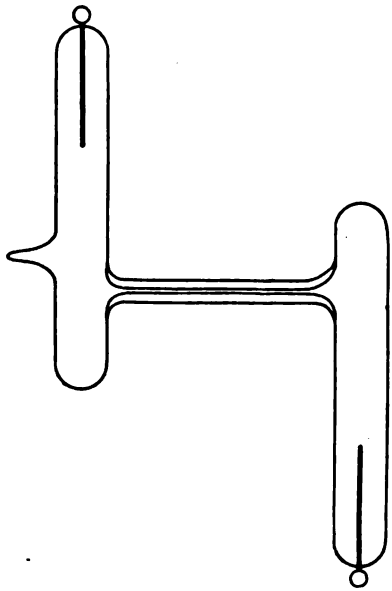

FIG. 138.

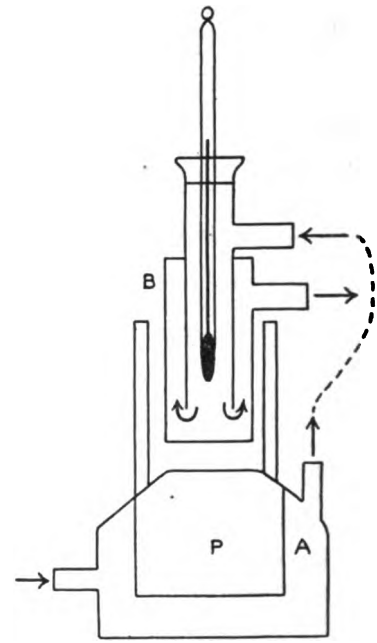

FIG. 139.

R is a prism for use with sodium light. It is removed when the Geissler tube is being used. *L* is a lens for use with the Geissler tube. It is removed when sodium light is used.

To use the instrument, place some of the required liquid in the cell *C*.

Illuminate the telescope slit and focus the cross-wires.

Place the cap on the cell, and from a thermostat pass water at the required temperature round the prism and through the cell-heater.

Illuminate the prism *R* by a sodium flame, turning *R* so as to throw a band of light on the slit in the cell cover.

Now turn the telescope round (with screw *K* slack) till a bright yellow band of light is seen. The upper edge of this corresponds with light which enters *P* as shown by the arrow in Fig. 139. Adjust this edge to the cross-wires (finally by clamping *K* and using *S*).

Having obtained several readings (at least 10, approaching the edge of the band from opposite directions alternately) find the mean and look up the

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refractive index from the angle i (measured) in the tables supplied by the maker with the instrument.

Corrections for temperature are also supplied.

Note.—In some types of instrument the prism is fixed and the "zero" must be taken as correct. In other forms several prisms (interchangeable) are supplied, for different refractive index ranges. After a prism has been fixed in position the telescope should be adjusted to zero by obtaining coincidence between the direct image of the cross-wires and their image reflected from the face of the prism nearest the telescope. (A small total-reflection prism is fixed in the telescope slit.) The slit must be well illuminated during the adjustment.

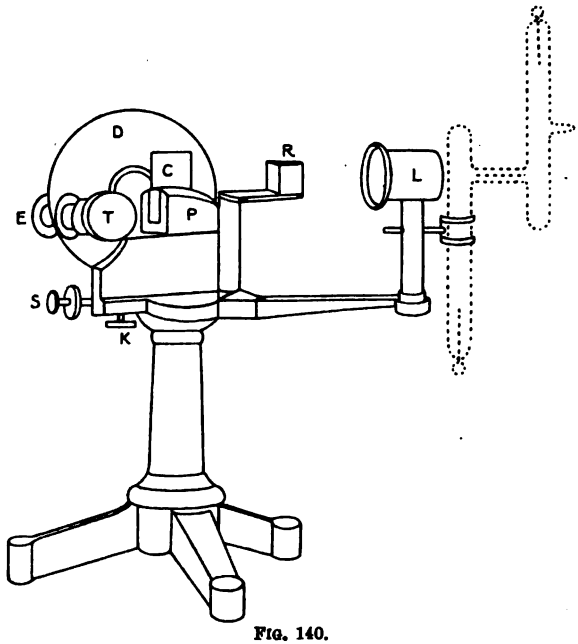

FIG. 140.

Determine the molecular refractivity of methyl and ethyl alcohol, ether, chloroform and carbon tetrachloride at 15°.

Also determine the molecular refractivity due to the CH_2 group in the case of formic and acetic acids at 25° C., and verify by finding the same from a study of benzene and toluene.

The principle on which this rests is the additive nature of the molecular refractivity, which is made up of the sum of the atomic refractivities of the atoms in the molecule.

It is a simple algebraic calculation therefore, after finding the molecular refractivities of various substances containing similar atoms, to deduce the atomic refractivities.

It is found that the benzene ring, double and triple bonds also, all have values of their own.

The principle may also be applied to solutions in a precisely similar fashion.

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CHAPTER VII.

ADDITIVE PROPERTIES OF THE MOLECULE—*Continued.*

Thermo-chemistry.—As practically all chemical reactions are exothermic or endothermic, *i.e.* occur with evolution or absorption of heat, thermo-chemistry is an important branch of physical chemistry as furnishing methods for determining energy changes.

Determinations may be classified as

(1) Heat of solution or dilution.
(2) Heat of neutralisation (and ionisation).
(3) Heat of combustion.
(4) Heat of formation.

To enable us to measure these quantities, we require

(1) A specification of the units.

(2) A knowledge of the specific heats of the substances reacting, and of the vessels in which the experiments are performed.

(3) The melting-points, boiling-points and latent heats of fusion and vaporisation of the bodies concerned.

Definitions.—The *unit* of heat is the calorie, or amount of heat required to raise one gram water through 1° C. from 15°-16° C. (The specific heat of water varies with temperature.)

The *large* calorie or kilo-calorie written "Cal." is a unit of 1000 calories, this unit being often more convenient owing to the smallness of the calorie.

Changes of temperature should be measured by means of an accurate thermometer graduated to hundredths of a degree C., *e.g.* a Beckmann, and the measurements are usually performed in polished "calorimeters" of silver, nickel, aluminium or copper placed on non-conducting stands inside one another as shown in the figure.

All calorimeters should be polished to prevent radiation as much as possible, and fitted with non-conducting covers.

The outer vessel should be double, and during the operation is kept filled with water at constant temperature. This in turn is surrounded by a jacket of felt. See Richards, *J. Am. Ch. Soc.*, 1910, p. 413, and Benedict and Higgins, *ibid.* p. 461.

The determination of melting- or boiling-points will be found elsewhere, while that of the specific and latent heats may be determined by methods based on what follows.

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Before any accurate determinations can be made, the water-value or aniline-value (or value in terms of whatever liquid is employed) of the apparatus, must be determined.

This is $$m_1s_1 + m_2s_2 + m_3s_3 + \ldots.$$

where m_1, s_1, etc., are respectively the masses and specific heats of the calorimeter, the thermometer and the stirrer. These are not determined separately, but as follows:

Fill the outer vessel with water and allow it to assume the temperature of the surrounding air (even if this takes a considerable time).

Now weigh the inner calorimeter, place in it about 250 c.c. pure distilled water, and weigh again.

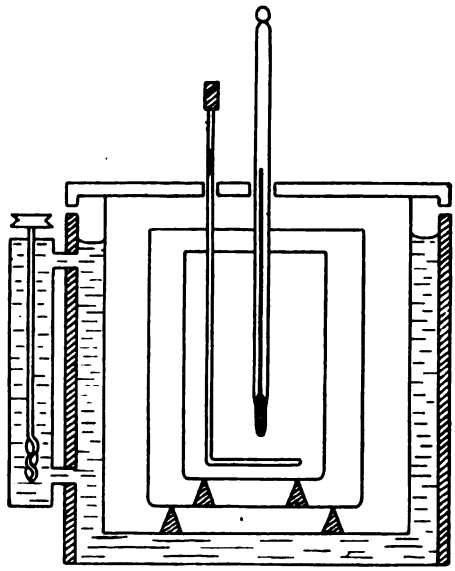

FIG. 141.

Put everything in position as in the diagram, meanwhile warming about 250 c.c. pure distilled water in a flask to 70° C. Place this flask in a vessel exactly similar to the calorimeter, with a thermometer dipping into it.

Take both temperatures every minute or half minute, stirring regularly and quietly the while.

At a certain moment, transfer the hot to the cold as quickly as possible, and continue to take readings of the temperature every period as before, continuing for at least 5 minutes.

The exact temperatures at mixing can be obtained from the extrapolation of the curves obtained.

Thus in the curves shown in Fig. 142, curve *a* gives the readings of the hot water; *b* of the cold water; *c* of the mixture.

These curves, when prolonged to meet the ordinate drawn for the time of mixing give the true temperatures x, y and z at which the hot, cold and mixture would have stood had mixing been instantaneous.

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Finally weigh the calorimeter proper to the nearest centigram to determine the amount of water added.

If W is the water value required, w_a the weight of hot water, w_b the weight of cold water, t_x, t_y, t_z the respective temperatures at time of mixing as found,

$$(W + w_b)(t_z - t_y) = w_a(t_x - t_z).$$

As the specific heat of water is not constant, the mean values for the ranges of temperature chosen should be taken.

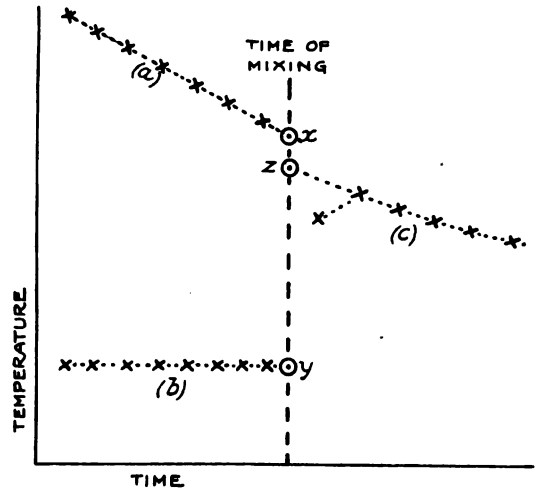

FIG. 142.

Table of Specific Heats of Water at Different Temperatures.

(Callendar, *Phil. Tr.*, 1902, 144.)

Temp	S.H.	Temp.	S.H.	Temp.	S H.
0°	1·0094	25°	0·9992	50°	0·9987
5°	1·0054	30°	87	60°	1·0000
10°	1·0027	35°	83	70°	16
15°	1·0011	40°	82	80°	33
20°	1·0000	45°	83	100°	74

The standard is the calorie at 20°.

For several experiments in which the bodies concerned do not mix with aniline, the latter may be used as the calorimetric substance, its specific heat being

$$0{\cdot}5156 + 0{\cdot}0004(t - 20) + 0{\cdot}000002(t - 20)^2 + \text{etc.}$$

Once the water value of the calorimeter is known, specific heats of solids or liquids may be determined in a precisely similar experimental method.

For determination of latent heats of fusion and vaporisation see Watson's *Practical Physics*.

Heat evolution or absorption is a strictly additive property, *Hess's Law* stating that:

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"The heat change from one state to another is independent of all save the initial and final conditions of the substance."

Thus, we may write the equation

$$2P,\ 5O = P_2O_5 + x \text{ Cal.},$$

meaning that when twice the atomic weight in grams of phosphorus burns in oxygen with the formation of one molecule of phosphorus pentoxide, x Cals. of heat are evolved.

Similarly,

$$P_2O_5,\ H_2O = 2HPO_3 + y \text{ Cal.}$$
$$2HPO_3,\ 2H_2O = 2H_3PO_4 + z \text{ Cal.}$$

Then the change 2P, 5O, $3H_2O$ to $2H_3PO_4$ would evolve $x+y+z$ Cals.

By determining, for example, the heats of solution or combustion of various allotropic forms of substance, we can determine indirectly the heat of transformation of one allotrope into another.

A thermochemical equation is expressed in the above manner, the full explanation of which will be found in theoretical text-books.

(1) **Heat of solution.**—This is the quantity of heat evolved or absorbed when one gram molecule of substance is dissolved in a stated number of gram molecules of a solvent. Care must be taken in the case of crystalline substances in which state of hydration the substance is originally taken, *e.g.* $CuSO_4.\ H_2O$ will have a different heat of solution from $CuSO_4.\ 5H_2O$, the difference being the **heat of hydration.**

Similarly the **heat of dilution** is the amount of heat evolved when one gram molecule of a substance is diluted from one given strength to another, or to such a great volume that the latter may be taken as infinity.

Determination of the heat of solution of sodium thiosulphate (potassium nitrate or any salt) **in water.** Take 10-15 grams of the salt, powder finely, and weigh in a test-tube if the nature of the salt permits, otherwise take the dried crystals and weigh in a stoppered or sealed vessel (*e.g.* if hygroscopic or efflorescent).

Place in an enclosure surrounded by water of known temperature, weigh the calorimeter and into it weigh some 500 grams of distilled water.

If possible, both the salt and the water are brought to the same temperature before mixing, but if not at air temperature, note the rate at which they cool.

When all is ready, transfer the salt quickly to the water and stir well, taking the temperature every half minute. Finally find the maximum temperature as described in the previous experiment.

For the greatest accuracy, it is necessary to know or find the specific heat of the solution of the salt of the final strength, though it is really very near unity.

If the salt is at a different temperature from the water, the specific heat of the solid must be taken into account. The working out of the result is obvious.

Determine the heat of hydration of $\begin{cases} ZnSO_4,\ 7H_2O \\ CuSO_4,\ 5H_2O \end{cases}$

(by experimenting with suitable quantities of the anhydrous and of the hydrated salts respectively).

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(2) **Determination of the heat of neutralisation of acids and bases. Heat of ionisation.**

Method.—250 c.cs. each of dilute solutions of the acid $\left(\frac{N}{2}\ HCl,\ H_2SO_4,\right.$ acetic acid, etc.$\left.\right)$ and of alkali $\left(\frac{N}{2}\ NaOH,\ NH_4(OH),\ KOH\right)$ are brought to the same temperature and mixed quickly with stirring. Temperatures are interpolated as before.

The specific heats of the resulting salt solution in the case of sodium chloride may be taken as 0·98; density 1·043 (*i.e.* of $\frac{N}{4}$ NaCl).

Theory and result.—(*a*) When caustic soda and hydrochloric acid are used a result of 13·7 Cal. will be found when using the equivalent amounts of each, but with ammonia and hydrochloric acid or with caustic soda and acetic acid other values will be obtained.

In the first cases, owing to the practically complete ionisation of NaOH and HCl, the equation of the reaction is

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + HOH.$$

The 13·7 Cals. therefore represent the heat of association of $H^{\cdot}$ and OH' ions.

If the solutions are not dilute, however, the true value is not obtained, as ionisation of the salts is not complete.

(*b*) In the latter cases, owing to the very incomplete ionisation of, *e.g.* acetic acid $\left(\frac{N}{2}\right.$ acetic acid has a degree of dissociation of 0·006$\left.\right)$ the difference between the result obtained and 13·7 Cal. will represent the *heat of ionisation* of the weak acid or base (the degree of ionisation being taken as practically nil within the limits of error).

The principal application of this is

The determination of the avidity of acids and bases (Thomsen's method). If a base and two acids or *vice versa* be present in a solution in equivalent proportions, the base will divide itself between the two acids in a certain ratio giving relative "avidities" or "strengths" of acids according to the ionisation of the latter. One method for the determination of this ratio is provided by Thermochemistry. (For other methods see Polarimetry, Electrochemistry and Chemical Kinetics.)

E.g.—**Determine the relative avidities of tri-chloracetic and nitric (or hydrochloric) acids.**—Find the heat evolved when 500 c.c. of $\frac{N}{2}$ solution of sodium trichloracetate reacts with the same quantity of $\frac{N}{2}$ hydrochloric acid, also when similar quantities of $\frac{N}{2}$ sodium chloride and trichloracetic acid react.

Suppose the proportion of sodium chloride transformed is x per unit quantity.

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Then $$NaClaq + CCl_3 . COOHAq$$
$$= xHClAq + xCCl_3 . COONaAq + (1-x)CCl_3 . COOHAq + (1-x)NaClAq + H_1,$$
where H_1 is the heat evolved,
$$CCl_3 . COONaAq + HClAq$$
$$= xCCl_3 . COONa + xHClAq + (1-x)CCl_3 . COOHAq + (1-x)NaClAq + H_2.$$

Now, in the *first* case, the heat evolved is that of neutralising x mols. of NaOH by x mols. chloracetic acid – heat of neutralising x mols. HCl by x mols. NaOH.

In the *second* case, it is that of neutralising $(1-x)$ mols. by HCl by NaOHAq – that from $(1-x)$ mols. of NaOH by $CCl_3 . COOHAq$.

$$\therefore \frac{H_1}{H_2} = -\frac{x}{1-x},$$

giving the ratio required.

If complications such as the formation of acid salts come in, they must be allowed for.

Suppose that Na_2SO_4 and $2HNO_3$ react together in dilute solution, and that x molecules of Na_2SO_4 are broken up, forming $2x$ mols. $NaNO_3$, then

$$Na_2SO_4 + 2HNO_3 = (1-x)Na_2SO_4 + xH_2SO_4 + 2xNaNO_3 + 2(1-x)HNO_3 + H \text{ Cal.}$$

H is obviously made up on account of a number of changes, in which the x molecules of H_2SO_4 may react with $1-x$ molecules of Na_2SO_4, to form the acid salt.

Thomsen gives the heat changes due to this as

$$Na_2SO_4Aq . x'H_2SO_4Aq = 3300\left(1+\frac{4}{5x'}\right)^{-1} \text{Cal} = \frac{16500x'}{5x'+4} \text{ Cal.}$$

Hence if we perform the experiment with (*a*) $2NaNO_3$ and H_2SO_4; (*b*) Na_2SO_4 and $2HNO_3$, and (*c*) use Thomsen's formula for the bye-action, the ratio may be worked out from substitution in an equation in a manner similar to the calculation for trichloracetic and hydrochloric acids.

(3) **Heat of combustion.**—The heat generated by the combustion of one gram-molecule of an organic body is known as the Heat of Combustion. From the value obtained, knowing the heat of formation of the products (CO_2 and H_2O and, at times NO_2) we can calculate the heat of formation of the body.

It must be remembered that different values must be expected according to whether the experiment is performed at constant volume or constant pressure.

Owing to the energetic nature of the combustion in some cases, and the changes of pressure and temperature which are likely to occur, the experiment is done in the Mahler "Calorimetric Bomb" (Fig. 143), in an atmosphere of compressed oxygen.

A strong, thick-walled vessel *A*, lined with porcelain or platinum, has a stout lid fitted to it, and in the lid, which screws on to a lead washer *B B* (to render everything air-tight) are two right-angled holes *C C'*, into which oxygen may be passed and which can be plugged by two screws *D D'* to keep out water.

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The holes are closed at the top by screw valves *E* and *E'*, *E* serving as one terminal of the electric current to be used.

Touching the bottom of *E* is a platinum tube, *H*, descending well into the calorimeter to allow of the passage of oxygen to the latter, and supporting a platinum crucible *I* into which the substance is placed.

G and *H* are connected electrically by a spiral of fine iron wire dipping into *L*. This serves as the igniting apparatus, being raised to a red heat by the electric current.

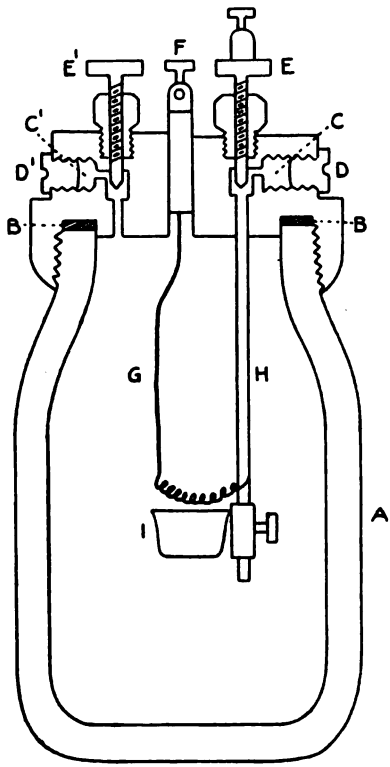

FIG. 143.

When filled, the bomb is lowered into the calorimeter, which is provided with a mechanical stirrer and a Beckmann thermometer, the remainder being as before.

To fill the bomb, unscrew the lid and place about 0·5 to 0·7 grams of the substance in question in the crucible in tabloid form; connect *G* and *H* by means of a weighed fine iron wire about 7 cm. long and 0·1 mm. diameter, wound in the form of a narrow spiral and made to dip into the crucible to touch the substance.

Rub a *little* vaseline around the lead washer and screw the lid firmly down. Feed in oxygen through *C*, *E* being loose and the valve *E'* closed. When a pressure of something just over 20 atmospheres is obtained, screw down *E*, disconnect the cylinder and screw in *D*, listening for any possible leaks, which must be avoided. Attach wires to *E* and *F* and lower the bomb carefully into the calorimeter containing a weighed amount of water (of such volume that it rises to the screws *D D'*).

Now allow everything to attain the same temperature, which should be arranged to be about 1·5° below air temperature, so that, if quantities be taken correctly, the final temperature will be about the same amount above it, thus minimising the effects of radiation.

The terminals are now joined through a switch to a battery of such potential difference that the iron wire takes fire in a second or two (to be determined by previous trial).

After everything has become steady, with the stirrer working, note the temperature every minute for about 10 minutes. Then close the circuit, noting the exact time.

The iron wire will ignite and break the circuit, but will have inflamed the substance in the crucible which will itself burn. Take readings every minute

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and note carefully the highest temperature attained. Continue to take readings every minute for 10 minutes, then remove the bomb from the calorimeter and empty it by unscrewing D', then E'. Remove the top, weigh any unburnt iron, clean and dry the apparatus.

The temperature may be calculated as before (interpolation) or from the expression

$$T = \tau + n\delta t' + \frac{\delta t + \delta t'}{2},$$

where T is the final temperature to be calculated, n the number of minutes from the time of ignition to the time of the determination of τ, the highest temperature attained, δt and $\delta t'$ the average rates of change of temperature during the periods before the ignition and after the attainment of the highest temperature respectively, taking the signs + or − into consideration.

The water value of the calorimeter cannot be determined very conveniently by the method given previously, but may be determined by burning a known mass of a body of known heat of combustion such as benzoic acid or naphthalene under the same experimental arrangements as those just described.

Data.—Heat of combustion of benzoic acid, 6·32 Cal. for 1 gm. (take 0·8 grams).

Heat of combustion of naphthalene, 9·69 Cal. for 1 gm. (take 0·5-0·75 grams).

Thus, determine the heat of combustion of benzene, salicylic acid or of camphor, and determine the heat of formation of camphor.

Calculation, $C_{10}H_{16}O + 27O = 10CO_2 + 8H_2O.$

Heat of combustion of $10CO_2 = 10 \times 96{\cdot}96 = 969{\cdot}6,$

$8H_2O = 8 \times 68{\cdot}36 = 546{\cdot}88.$

So $(C_{10}, H_{16}, O) + (C_{10}H_{16}O : 27O) = 1516{\cdot}48$

$$(C_{10}, H_{16}, O) + \frac{M}{w}h = 1516{\cdot}48,$$

where M is the molecular weight, w the amount taken, h the number of calories measured.

Hence (C_{10}, H_{16}, O) is determined. (Heat of formation.)

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CHAPTER VIII.

ADDITIVE PROPERTIES OF THE MOLECULE—*Continued.*

Spectroscopy.—The study of the spectrum in the hands of Baly, Desch and Collie has yielded many results of highest importance, the bright spectral lines emitted by gases and vapours yielding a means of identification of elements not only in the laboratory but also in astronomical work.

The spectrometer.—This instrument consists essentially of a slit *S* illuminated by a source of light and an arrangement of lenses (Fig. 144).

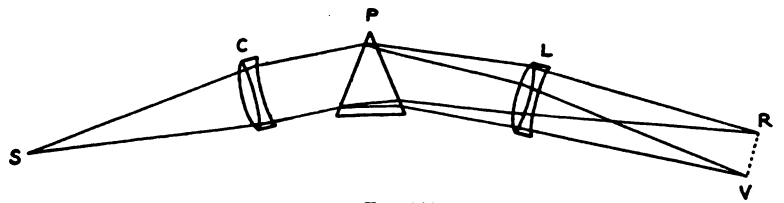

FIG. 144.

A lens *C*, termed a "collimator," is placed such that *S* is in its focal plane, thereby producing a bundle of parallel rays. These are refracted by means of a dense lead glass prism, set in the position of minimum deviation for mean (sodium *D* line) rays, into a number of coloured parallel beams which are in turn collected by a second lens. The image or spectrum thereby produced is viewed with the aid of an eye-piece with cross-wires fixed at *R V*. The lens *L* and eye-piece at *E* form a telescope which is capable of rotation around a circular scale in a horizontal plane, and is fitted with a vernier.

To adjust the spectrometer, remove the prism, turn the telescope round towards a distant object, focus the cross-wires with the eye-piece and then the telescope itself on a distant object. It is then adjusted for the reception of parallel rays.

Illuminate the slit, and looking directly at it through the collimator and telescope, bring the slit into focus by racking it nearer or farther from the collimator as the case may be.

In some spectrometers the prism table requires no adjustment; in others, it is provided with three levelling screws, but in any case it can be rotated in its own plane.

Place the prism on this table with the refracting edge towards the collimator, illuminate the slit with sodium light (all other light being excluded), and rotate the telescope in order to receive the reflected image. Now carry

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the telescope round to the other side to get the image reflected from the other face, thus discovering whether or no the prism is in adjustment. If it is not, it must be adjusted by the levelling screws and clamped lightly to its table. For a full account of the adjustment and its theory see Watson's *Practical Physics*, pp. 292 ff.

Now rotate the prism until a refracted image of the slit is seen with the eye on looking through the prism, and continue to rotate until the position of minimum deviation is reached. Adjust this position accurately by looking through the telescope and moving the latter until the image is seen; rotate the prism, following the image with the telescope until this image appears to cease moving forward and starts to move back in its original direction. The reading of the deviation may be taken by causing the image of the slit and vertical cross-wire to coincide, then reading the circular scale and vernier.

As a source of light, we may use either a vertical Geissler tube, or the salts of certain metals introduced into the Bunsen flame as described in a previous experiment, but care must be taken to have a narrow slit.

Calibration of the spectrometer.—Bright lines of known wave length (see table) are used, suitable ones being mentioned here.

The wave lengths are expressed in micro-millimetres ($\mu\mu$ = unit of 10^{-6} mm.), or in Ångstrom units (10^{-7} mm.).

Table of Wave-lengths in Ångstrom units.

Substance.	Colour.	Wave length.
Sodium - - - -	yellow.	5890
,,	,,	5896
Potassium - - - -	red.	7668
,,	violet.	4047
Lithium - - - -	red.	6708
,,	orange.	6104
Thallium - - - -	green.	5351
Hydrogen - - - -	orange red (C).	6563
,,	blue green (F).	4861
,,	blue (H).	4341
Helium - - - -	orange red.	6678
,,	yellow.	5876
,,	green.	5016
,,	blue green.	4922
,,	indigo.	4472
Copper (arc) - - -	yellow.	5780
,, ,,	1st green.	5290
,, ,,	2nd ,,	5220
,, ,,	3rd ,,	5153
,, ,,	4th ,,	5105
,, ,,	blue.	4651
Mercury (vapour lamp) -	blue.	4916
,, ,, ,,	,,	4358
,, ,, ,,	violet.	4078

The angular deviations of a number of well-distributed lines are read off on the scale and vernier when the images coincide with the cross-wire, and a curve is drawn, ordinates representing wave length, abscissae angular deviations.

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From this curve the wave length of any line whose deviation is measured can be read off by interpolation. Naturally the curve only holds good for the given prism.

Space will not permit of a lengthy discourse on spectroscopy; the student is referred to Baly's *Spectroscopy* and other works.

An indication of the possibilities, however, is given.

1. **Analysis.**—Knowing by experience certain spectrum lines produced from salts of sodium, potassium, lithium, strontium, calcium, barium, thallium, etc., one can with a pocket spectroscope or an instrument set up as described, identify mixtures of these substances.

For accurate work a measurement is made of the deviation of the lines with subsequent reference through the curve to a table of wave lengths.

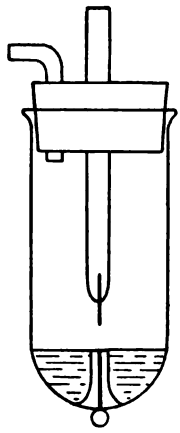

FIG. 145.

The chloride is the best salt, and this if introduced on a platinum cage into a Bunsen flame produces the requisite light.

Should the salt be insoluble, it can be fused with sodium carbonate, and the resulting carbonate moistened with hydrochloric acid. Examine salts of Ca, Sr, Ba, Li, Tl, Na, K, etc.

Metals, if made the terminals of an induction coil with small spark gap, or the terminals of an electric arc, give characteristic lines which can be measured. Care must be taken in many instances not to let poisonous vapours escape into the air.

Examine Geissler tubes of rarefied gases under electric discharge.

Spark spectra of solutions of $MgCl_2$, $SrCl_2$, NaCl, etc., may be examined by volatilising the solution from a capillary by means of a spark from a coil (Fig. 145).

2. **Study of absorption spectra.**—When a beam of white light passes through a coloured solution, the latter cuts out certain rays, dark bands or lines being seen on examining the spectrum.

Such bands or lines are characteristic and afford identification or information concerning the structure of organic and inorganic substances.

Study the effect of dilution on solutions of potassium permanganate, potassium dichromate, uranous salts, copper and cuprammonium salts, iodine in alcohol and in potassium iodide solution, and suspensions of haemoglobin, using the light of a carbon or iron arc with close terminals.

Also study and measure the Fraunhofer lines of the solar spectrum, and identify some of the elements. Examine the absorption spectra of N_2O_4 and iodine vapour, also the maximum absorption of coloured salts at certain dilutions.

The student is referred to text-books for further ideas and experimental exercises.

3. **Study of anomalous dispersion.—Demonstration of Sellmeier's theory.**—See Wood's *Physical Optics* for interesting experiments on this subject.

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CHAPTER IX.

OPTICAL ACTIVITY.

Polarisation.—When a ray of light passes through a crystal of Iceland spar, it is doubly refracted unless the ray travels along an axis of symmetry; the two rays produced are each such that the transverse vibrations of the luminiferous ether are in one plane only.

Each ray is then said to be "plane polarised," the plane of vibration of one ray being perpendicular to that of the other. If the crystal be cut diagonally, and the two pieces cemented together with a layer of Canada balsam (Fig. 146), one ray passes through the instrument (the ray of less refraction, *IA*); the other, however, *IB*, of greater refraction, finds the layer of Canada balsam such that the refractive index of this new material is less than that of the spar. Hence the ray strikes very obliquely on a medium of less refractive index, relatively to that ray, than the Iceland spar through which it is travelling, and so becomes totally reflected.

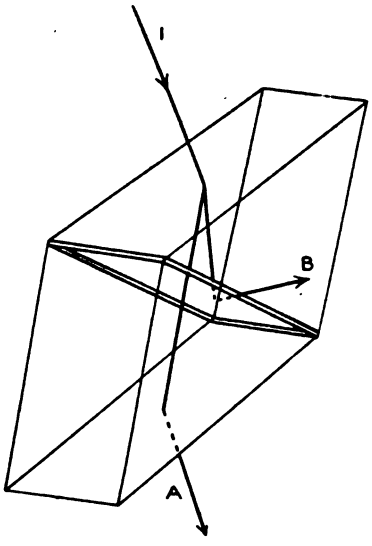

FIG. 146.

The system is called a "Nicol's Prism," and is used for plane-polarising light.

If another Nicol's prism be placed parallel to the first, the ray which has travelled through the one also passes through the other, but if the second instrument is rotated round the direction of the ray until it is at right angles to the first Nicol, the ray cannot get through, thus causing total extinction.

The first Nicol is called the polariser, the second the analyser.

Many organic substances in solution or by themselves possess the power of rotating the plane of polarisation, so that if interposed between crossed Nicols, the field of view is no longer dark.

If the analyser has to be rotated to the right, the body is called "dextrorotatory," if to the left, "laevorotatory," the apparatus for the measurement of this being termed the *polarimeter*.

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Laurent's half shade device.—Instead of relying on the total extinction of light, which cannot be determined with accuracy, various devices are used to increase the sensitivity.

The "half shade" device consists in arranging one portion of the field of view so that the plane of polarisation is rotated slightly to the left, while in the other portion of the field the plane is rotated equally to the right, monochromatic (*e.g.* sodium) light being employed.

Thus, in Fig. 147, if the analyser be rotated ⊥ to *LO*, *LO* and *RO* being the directions of the projections of the planes of polarisation in the two halves of the field, the field *ABOC* will be dark, *A'BOC* relatively light.

If the analyser be rotated the fields will counter-change, both sides being of equal intensity when the analyser is ⊥ to *OB*.

In the Laurent half shade, this effect is achieved by placing in one half of the field a plate of quartz cut parallel to the optic axis, such that through

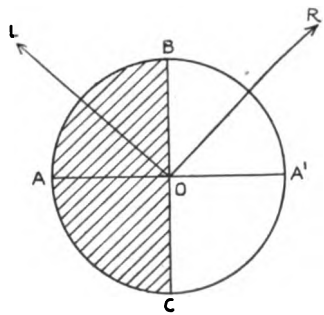

FIG. 147.

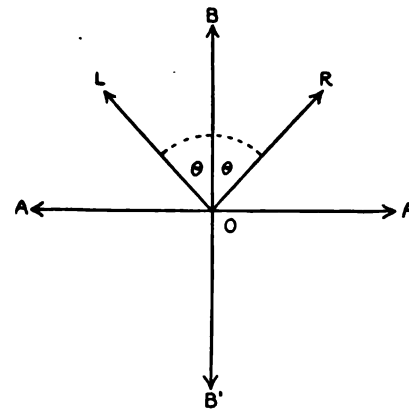

FIG. 148.

this quartz the vibrations of the ether are retarded in one plane more than in that at right angles to the latter by 180° of phase or half a wave length.

Thus, suppose *OB* and *OA* (Fig. 148) are the resolved simultaneous directions of a portion of wave *OL*. Suppose in the plane *AOA'* a retardation of half a wave relatively to that in the direction *BOB'* takes place. Then simultaneous directions of the motion will be *OB* and *OA'*, which compound into *OR*, making the same angle θ with *OB* as *OL* did before the wave travelled through the quartz plate.

The angle *BOR* can be regulated, the smaller it is the more sensitive is the change, although less total light is let through, giving a greater strain to the eye. The experimenter must regulate this to suit himself.

The Bi-quartz plate is another device. It consists of two semicircular plates of quartz of equal thickness cut from dextro and laevo rotatory crystals, and fixed symmetrically to the principal plane of the polariser.

The theory and practice is similar to the above, equal tints being obtained in the field if white light is used; equal illuminations if monochromatic light is employed.

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Other devices also exist, but in all cases they depend on the equal illumination of parts of the field of view. Thus Lippich, by the use of two auxiliary Nicols, divides the field in three parts, causing less eye-strain and more accurate adjustment.

The polarimeter.—The arrangement of the apparatus is shown diagrammatically as follows:

S is a source of light, C a collimator, N_P the polariser which can be rotated between limits by means of the adjusting lever A.

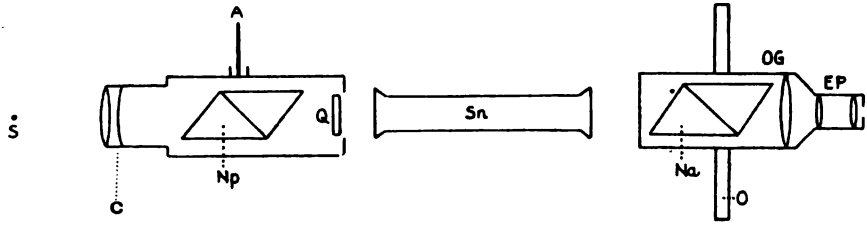

FIG. 149.

Q is the bi-quartz or half shade, S_n the tube of solution or optically active liquid either 10 or 20 cm. in length.

N_A is the analyser, and this with a telescope is attached to a holder rotating as a whole, rotation being measured on a fixed circular scale O (shown in section) by means of a sliding vernier fixed rigidly to the holder carrying N_A.

A small lens is generally fitted in front of the vernier to facilitate readings.

In some instruments, instead of a circle, a "Soleil's compensator" is used. This consists of two wedges of optically active quartz of equal angle arranged to slide over one another producing a plate of varying thickness, measurements being made by a micrometer screw regulating this sliding (Fig. 150).

FIG. 150.

The polariser is arranged so that the portions of the field of view are of equal illumination when the quartz wedges are immediately one below the other.

The introduction of the solution will necessitate the adjustment of the wedge by increasing or decreasing the thickness. The scale should be calibrated previously.

To use the instrument, arrange it such that the source of light is at a distance from the collimator approximately equal to the latter's focal length.

Now focus the eye-piece so that the half shade is seen clearly. Rotate the analyser until there is equal illumination of the field, adjusting the sensitivity to the most convenient value consistent with clear vision.

(Note that another position of the analyser at 90° to the required position will give equal illumination—this occurs when the plane of polarisation given by the analyser is nearly that given by the polariser in the two halves of the field—this position must be avoided.)

The zero of the instrument must be determined before measurements are made—this is effected by filling the tube with pure distilled water, reading off the scale and vernier when the equal illumination is obtained, and taking

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the mean of ten readings, approaching the position from either side alternately. Readings to the left are to be taken as negative, to the right as positive, and the requisite corrections to subsequent readings noted.

Rotation of the plane of polarisation.—The amount of rotation is proportional to the concentration of a solution and the length of it viewed. It also depends on the temperature and the wave length of the light, so that monochromatic light should be employed.

The **specific rotation** of a solution of active body in an inactive solvent is the rotation produced by unit mass of substance in unit volume of solution when one decimetre length of solution is employed. It is denoted by the symbol $[\alpha]_D^t$ at $t°$ C. when the sodium D line is the source of illumination.

Thus if x grams dissolved in 100 c.c. of solution produced a rotation of $d°$ through l dms. of length of liquid,

$$[\alpha]=\frac{100d}{lx} \text{ or more accurately } \frac{100d}{lx\rho},$$

where ρ is the density of the solution.

The **molecular rotation**

$$[m]_D^t=M\times[\alpha]\left(\text{or } \frac{1}{100} \text{ of this}\right),$$

where M is the molecular weight of substance.

In the case of a single homogeneous active body such as turpentine,

$$[\alpha]=\frac{d}{l\rho}$$

using terms similar to the above.

Dextrorotation is regarded as positive, laevorotation as negative.

Determine the concentration of a cane sugar solution after finding $[\alpha]_D^{15}$ for cane sugar. Firstly to find $[\alpha]_D$.—Powder finely 10-12 grams of recrystallised cane sugar, and dry over conc. sulphuric acid in a desiccator for 10-12 hours. Make a solution in cold, pure distilled water of about 10 grams weighed out accurately, the solution being made in a 100 c.c. flask. Let it stand for some time till solution is complete, make up the volume to the mark after shaking; shake again.

Now, after finding the zero of the instrument, rinse a tube with the sugar solution, fit the cap with the glass-plate on one end, pour in the solution, and allowing no bubbles to be enclosed, slide on the other glass-plate and screw in the cap. Observe the rotation and calculate the result, noting the temperature of the experiment.

N.B.—Never leave the tube full of liquid, otherwise it may be cracked by expansion.

For cane sugar, verify that

$$[\alpha]_D^t=66{\cdot}5-0{\cdot}0184(t-20).$$

Having found α_D^t, use the result to calculate the strength of the solution of unknown concentration, thus:

If the solution has P grams of active substance and E grams solvent, the solution having the density s, then

$$P+E \text{ grams solution occupy } \frac{P+E}{s} \text{ c.c.}$$

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Hence 1 c.c. solution contains $\frac{sP}{P+E}$ gms. substance ;

$$\therefore\ [\alpha]=\frac{d}{l\frac{Ps}{P+E}}=\frac{d}{l},\ \frac{P+E}{Ps}$$

or if p is the percentage concentration,

$$p=\frac{100P}{P+E};$$

$$\therefore\ [\alpha]=\frac{d100}{lps},$$

$$p=\frac{100d}{l[\alpha]s}.$$

Determine the specific and molecular rotation of turpentine, lactic acid, or any active organic body (all of which contain an asymmetric carbon atom).

At temperatures other than atmospheric, a special tube provided with a jacket similar to a Liebig's condenser is employed (Fig. 151).

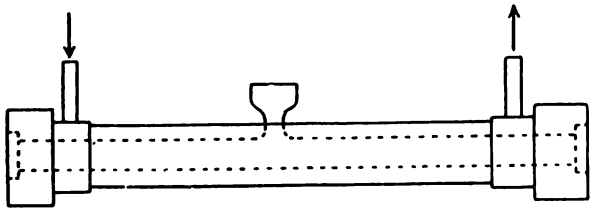

FIG. 151.

Determine the rate of inversion of cane sugar by dilute sulphuric acid.—For invert sugar $[\alpha]_D^t=19^0{\cdot}657+0{\cdot}0361c-0{\cdot}304(t-20)$

where c is the weight in grams per 100 c.c., as the value varies according to the concentration.

Remember that when inverting cane sugar

$$C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6+C_6H_{12}O_6,$$

342 grams cane sugar = 360 grams invert sugar.

$$c=\frac{360}{342}\text{ wt. of cane sugar per 100 c.c.}$$

The rate of reaction is proportional at any time to the amount of sugar not yet inverted.

If A is the original amount of cane sugar, x the amount inverted after a certain time, t the time from the commencement of reaction

$$\frac{dx}{dt}=K(A-x)$$

where K is a constant.

$$\log\frac{A}{A-x}=0{\cdot}4343Kt,\ \text{(see Chapter XII)}$$

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or
$$\frac{1}{t}\log\frac{A}{A-x}$$
is a constant.

Suppose α is the original rotation,
α_∞ ,, rotation at complete inversion,
α_x ,, ,, after x has been inverted.

then
$$\alpha_x=\alpha\frac{A-x}{A}+\alpha_\infty\frac{x}{A},$$
from which
$$\frac{A}{A-x}=\frac{\alpha-\alpha_\infty}{\alpha_x-\alpha_\infty};$$
$$\therefore\ \frac{1}{t}\{\log(\alpha-\alpha_\infty)-\log(\alpha_x-\alpha_\infty)\}=\text{a constant.}$$

To test the accuracy of this, dissolve about 16 grams of pure sugar in 100 c.c. pure distilled water, and place in a constant temperature bath (temp. of room), likewise 50 c.c. of an approximately normal solution of sulphuric acid.

When all is at constant temperature, mix the solutions, shake, and at once take a reading in the polarimeter of the activity of a portion of the solution. As the tube if 20 cm. long will probably hold about 16 c.c., nine readings can be taken at suitable intervals, but if more solution be mixed beforehand the number of readings can be extended or made more frequent.

By this means, determine the relative strengths or **Avidities of sulphuric and hydrochloric acids.** (These are proportional to the reaction constant found as described on the last page. Compare with the thermochemical method.)

Optical isomerism of organic acids.

Every optically active body has one or more "asymmetric" carbon atoms, *i.e.* carbon atoms to which are attached four different atoms or groups (see theoretical books). The reverse is not necessarily true for the following reasons:

1. The substance may consist of exactly equal quantities of the *d*- and *l*-forms. This is the case in synthesised products.

Such a mixture is termed "inactive" (*i*-) or racemic (*r*-), and need by no means have the same physical constants as the individual active forms.

Thus: *r-Tartaric acid.*—Solubility 1 in 5·8 water at 15°. Loses water of crystallisation on heating to 110°, the anhydrous acid melting at 205°.

d-Tartaric acid.—Solubility 1 in 0·76 water at 15°. M.P. 167-170°. Destroyed by *penicillium glaucum* (Pasteur, *C.R.* **51**, 298).

l-Tartaric acid.—Same as for *d*-acid but *not* destroyed by *penicillium glaucum*. For the 20 % solution of each,
$$[\alpha]_D^{10}=9{\cdot}96,\qquad [\alpha]_D^{20}=11{\cdot}57.$$

2. The substance may possess two equal asymmetric carbon atoms as in tartaric acid. If these neutralise one another, an "*internally compensated*" or "*meso*" form results. This, being a true compound, cannot be resolved. Meso-tartaric acid loses 1 H_2O at 100°, then melts at 140°.

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CHAPTER X.

ELECTROCHEMISTRY.

1. **Definitions.**—Ohm's Law. When a current of electricity flows through a conductor, the strength of the current is given by

$$c = \frac{e}{r},$$

where i represents the current in *ampères*, e represents the potential difference in *volts*, r represents the resistance of the circuit in *ohms*, the same law being obeyed in electrolytes as in metallic conductors.

An *ampère* is that strength of current which liberates 0·0000104 grams of hydrogen (or the equivalent amount of copper) from solution in 1 second. This weight of an element is called its **electrochemical equivalent.**

The quantity of electricity passing through a circuit when one ampère has passed for one second is termed the *coulomb*; this charge when collected and insulated repels a similar insulated charge at a distance of 1 cm. with a force of *one dyne.*

The *ohm*, or practical unit of resistance, is the resistance offered by a column of mercury 106·3 cm. long and of 1 sq. mm. cross section at 0° C. (The ultimate definition rests on mechanical grounds.)

The *volt* is that electric pressure or potential difference which forces a current of 1 ampère through a resistance of 1 ohm.

The **specific resistance** of a conductor is the resistance of 1 cm. length of cross section 1 sq. cm., the **specific conductivity** being the reciprocal of this, and denoted by K.

In electrochemistry, we have to deal, not so much with the conductivity of the solvent as with that of the solute, therefore we require an expression bringing into account the amount of dissolved substance.

The quantities used are:

(1) Equivalent conductivity.
(2) Molecular conductivity.

The **equivalent conductivity** is that of a solution containing 1 gram-equivalent of the dissolved substance when placed between electrodes of indefinite size and 1 cm. apart. It is denoted by the symbol λ.

The **molecular conductivity** is that of a solution containing 1 gram-molecule of the substance as above, denoted by μ.

The relation between these derived functions and the specific conductivity is $\mu = Kv$, where v is the volume in c.c. containing 1 gram-molecule.

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In general, the volume of solution between the electrodes will not be v, but something much smaller, so that in a particular cell with electrodes, the conductivity will stand to the specific conductivity in a definite ratio depending on the capacity of the vessel and the electrodes. This ratio is the constant of the cell "c," which must be determined.

2. **Measurement of resistance and conductivity.**—There are two methods for determining these for electrolytes.

(1) The Wheatstones Bridge method.
(2) The Quadrant Electrometer method.

Method (1) is almost universally employed, and therefore described here.

The diagrammatic arrangement is shown in Fig. 152.

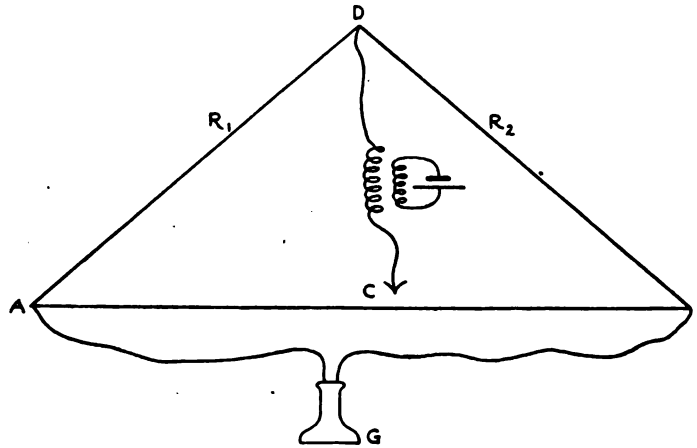

FIG. 152.

ab is a long uniform wire or set of resistance coils, R_1 a standard resistance or box, R_2 the cell containing the electrolyte (see below), and c a sliding contact for the battery terminal on the bridge; G is a galvanometer.

When $R_1 : R_2 :: ac : cb$, there is the same fall of potential at a as at b, and no current flows through the galvanometer, so that

$$R_2 = \frac{R_1 cb}{ac}.$$

In practice, however, the battery or cell and galvanometer are not suitable owing to the polarisation at the electrodes of the electrolytic cell when a direct current passes through the latter.

In place of the battery or cell the secondary of a small induction coil is used, the galvanometer being replaced by a telephone. When the point of balance is obtained, no current passes through the telephone so that silence ensues, or at any rate a well-defined minimum of sound. The telephone and coil are interchanged from the usually accepted positions, the coil being connected to the sliding contact instead of the telephone, so that the coil is only used when contact is made. If the telephone were connected to the slide, noises would be produced when making and breaking contact. In any case the telephone must be some distance from the coil.

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The **bridge wire** is a uniform wire 1-2 metres in length made of constantin or iridium-platinum alloy. A sliding contact is arranged to make contact at any point of the wire and also to indicate the reading of the same by an overlapping pointer. For convenience sake the wire is often arranged on a rotating drum, the position of the contact being read off on a circular scale at the end.

The **induction coil** should be small and able to give a high-pitched note, this being easily heard in the telephone. The current through the coil should be regulated by a variable resistance to prevent undue noise.

The resistance box should be of the ordinary type with wires coiled such that their ends are in contact with brass blocks, the coils being wound in forward and reverse spirals to prevent the formation of magnetic fields.

The plugs making contact with the brass blocks when the resistance coils are not required in use must be put in firmly and screwed slightly round;

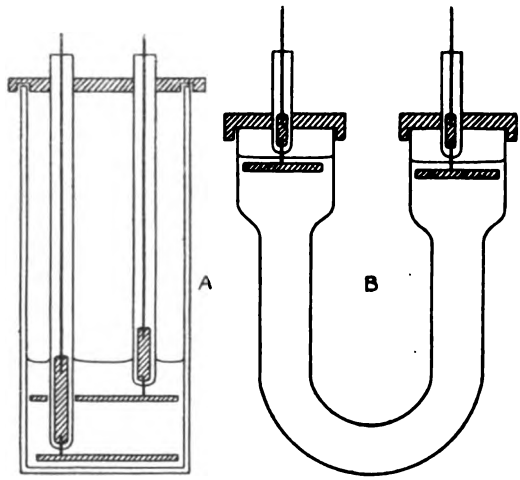

FIG. 153.

they should also be kept free from grease by wiping with a petroleum rag if necessary.

The **cell** (Fig. 153).—Electrolytic cells vary in size and shape. In general the resistance should be large (100 ohms or over) and the electrodes large. An air-tight cover is provided, without which the cell is useless, as the conductivity water will rapidly absorb enough carbon dioxide to increase its conductivity.

The vessel is of glass, steamed for some time before use to free from alkali.

Various shapes are employed, but in all cases it is advisable to use large platinum electrodes and coat the latter with finely divided platinum before use, provided that no catalytic action is likely to result.

This is done by immersing in Lummer's solution (3 gr. H_2PtCl_6 in 100 c.c. water with 0·02 gr. lead acetate) after cleaning with dilute sulphuric acid and potassium dichromate, passing at the same time the current from two accumulators in series.

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The resistance is regulated so that there is a slight evolution of gas and the direction of the current is changed from time to time. When thoroughly black and velvety on the surface, remove the electrodes to a dilute sulphuric acid solution, and pass a current for some time to remove adhering platinum solution. Wash in tepid water, changed frequently, then place them in their cell with distilled CO_2-free water, and determine the resistance with changes of water till constant. Preserve in air-free water when not in use.

The whole must be done in a constant temperature enclosure, as a change of one degree may alter the resistance by 2 per cent.

Operation.—The telephone is held to the ear (if necessary, the other ear can be plugged to keep out the sound of the coil) and the comparison of the electrolytic resistance with the known resistance is carried out as usual by the Wheatstone's Bridge. The standard resistance should be arranged so that the point at which the telephone ceases to give any or more than minimum sound on making contact with the bridge wire is reasonably near the middle of the bridge. Hence the adjustable resistance will be fairly large; perhaps several thousand ohms.

The point of contact must be determined several times approaching from either side, the mean reading of at least ten trials being taken.

Avoid an indefinite minimum by

(1) Short circuiting the coil by means of a fine wire.
(2) Inserting a condenser in parallel either with the cell or the resistance box.
(3) Replatinising the electrodes if necessary.

Results should agree to within 0·5 per cent.

3. **Determination of the constant of a cell.**—As mentioned above, the constant of the cell is determined by finding the resistance, and therefore the conductivity of a solution of which the specific conductivity is known.

If for two liquids of specific conductivity κ and κ_1 the resistances in the same cell were ω and ω_1 respectively, then $\omega\kappa = \omega_1\kappa_1 = C_1$ the constant.

C is here numerically equal to the specific conductivity of a solution which in the given vessel would have a resistance of 1 ohm. The most convenient standard liquid to use is $\frac{N}{50}$ KCl, the conductivity of which has been accurately determined by Kohlrausch, Holborn and Diesselhorst, and is given below.

Temp.	κ	Temp	κ	Temp.	κ
10° C	0·001994	17° C	0·002345	24° C	0·002712
11	2043	18	2397	25	2765
12	2093	19	2449	26	2819
13	2142	20	2501	27	2873
14	2193	21	2553	28	2927
15	2243	22	2606	29	2981
16	2294	23	2659	30	3036

This solution is accurately made up, using "conductivity water" (see below) and the purest obtainable salt. The electrodes are rinsed with some

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of the solution and introduced into the cell containing sufficient of the solution to cover them well. The whole is then placed in a thermostat. The resistance is then determined as already described.

If at balance $R : \omega :: x : y$ (x and y being the wire lengths) then

$$\omega = \frac{Ry}{x},$$

and κ (from the table) $=$ specific conductivity,

$$= \frac{C}{\omega} = \frac{Cx}{Ry}.$$

Hence $$C = \kappa\omega$$

$$= \frac{\kappa Ry}{x}.$$

Preparation of conductivity water.*—Fit up an apparatus consisting of (1) a steam boiler in which steam is generated from *distilled* water and bubbled into (2) a flask containing some dilute permanganate and sulphuric acid. This also is kept boiling and the steam from it is bubbled into (3) dilute caustic soda solution boiling in another flask. The steam from this is condensed in a *tin* condenser and collected in a thoroughly-steamed Jena glass flask. It should not be kept long, or exposed to the air at all, as CO_2, or alkali from the glass, etc., will be dissolved and increase the conductivity.

The first and last quarters of the distillate above should in any case be rejected.

4. **Determination of the equivalent or molecular conductivity of electrolytes.**—Make a normal solution of the required electrolyte in conductivity water. Accurately adjust the strength by titration if necessary. Set it in a Jena glass flask with a stopper, in the thermostat at the required temperature (18° or 25° usually). Also place in the same thermostat a stoppered flask of conductivity water.

Clean the conductivity cell, wash both it and the electrodes with conductivity water, and dry in the steam oven.

Measure the conductivity of 20 c.cs. of the prepared solution, first allowing the whole apparatus to attain the temperature of the thermostat and removing any bubbles which may adhere to the electrodes. (Take the mean of 10 readings.)

To dilute the solution to half strength, remove 10 c.cs. by means of a *withdrawal* pipette, and put in 10 c.cs. of conductivity water by means of a *delivery* pipette. *Always remember this precaution.*

Expose the solution to the air as little as possible during the determinations, which will otherwise be useless as the solution becomes very dilute.

Continue until a dilution of $\frac{N}{1024}$ is reached.

It is then advisable to perform a fresh series of experiments to eliminate errors due to dilution.

(*a*) *To show that the equivalent or molecular conductivity increases to a maximum with the dilution.*—If v is the volume in c.cs. of solution containing

* See also Bourdillon, *J.C.S.* 1913, 791.

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one gm.-equivalent of the electrolyte and κ the specific conductivity, then the equivalent conductivity, λ, is given by

$$\lambda = \kappa v.$$

Similarly the molecular conductivity μ is given by

$$\mu = \kappa v.$$

(v in this case being the volume in c.cs. containing one gm.-molecule.)

It will be found that on dilution the molecular (or equivalent) conductivity increases to a maximum, further dilution having no effect.

Suitable electrolytes to use for this experiment are:

Hydrochloric acid, sodium hydroxide (dissolve sodium in conductivity water in an atmosphere free from carbon dioxide), sodium chloride and strongly dissociated electrolytes generally.

HCl at 18°.		NaCl at 18°.	
v	μv	v	μv
1000	278	1000	74·4
10,000	324	10,000	92·5
100,000	342	100,000	102·8
500,000	345	1,000,000	107·8

(*b*) *Ostwald's dilution law.*—The law according to which the conductivity of an electrolyte thus increases to a maximum follows by applying the Mass Law to ionisation.

If $AB \rightleftharpoons A + B''$, and if at equilibrium the degree of ionisation is α, and the dilution v, it follows at once that

$$K \cdot \frac{1-\alpha}{v} = \frac{\alpha}{v} \times \frac{\alpha}{v},$$

or

$$\frac{\alpha^2}{(1-\alpha)v} = K \text{ (a constant).}$$

This constant is the "ionisation constant" of the electrolyte. In the case of acids or bases it gives a measure of their "strengths" or "avidities," thus:

Solving the above equation for α we have $\alpha = \sqrt{Kv}$ if α is small (weak acids and bases). Then for two acids (or bases) at the same dilution

$$\frac{\alpha}{\alpha'} = \sqrt{\frac{K}{K'}}.$$

In the experiment, $\alpha = \frac{\lambda_v}{\lambda_\infty}$ or $\frac{\mu_v}{\mu_\infty}$ so $K = \frac{\mu_v^2}{\mu_\infty(\mu_\infty - \mu_v)v}$.

The values of K for several acids are given in the following table:

Acids.	100 K at 25°.
Acetic	0·0018
Chloracetic	0·155
Dichloracetic	5·14
Trichloracetic	121
Benzoic	0·006
Bases.	
Ammonia	0·0023
Methylamine	0·050
Trimethylamine	0·0074

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From the table it can thus be calculated that in equimolar solutions of acetic and of monochloracetic acids the ratio of hydrion concentration is 1 : 9·3.

It should be stated that Ostwald's dilution law does not hold for salts or for *strongly* ionised acids and bases. Any of the above substances may be used to prove the law.

Van't Hoff proposed an empirical law for highly ionised electrolytes,

$$\frac{\alpha^3}{(1-\alpha)^2 v} = K.$$

Determine the conductivities of any of the above acids or bases at several different dilutions. Look up λ_∞ or μ_∞ from a table, as these are not found by experiment, the dilution being so great for weak electrolytes that the error becomes greater than the quantity being determined.

Substance.	λ_∞ **at 25°.**
Acetic acid	352
Chloracetic acid	360
Dichloracetic acid	358
Trichloracetic acid	356
Benzoic acid	381
Ammonium hydroxide	244
Methylamine	232

5. **Determination of the basicity of acids.**—Ostwald found that the *sodium* salts of weak acids (organic acids) show a curious conductivity property, viz. that

$$\lambda_{1024} - \lambda_{32} = 10B. \quad (B = \text{basicity of acid.})$$

This may be utilised for finding the basicity of acids.

Make a $\frac{N}{32}$ solution of the sodium salt of benzoic, tartaric, citric, etc., acid; it is obtained free from CO_2 by putting in a 100 c.c. flask the exact quantity of caustic soda solution (prepared by sodium in a CO_2-free atmosphere acting on conductivity water) that will make a $\frac{N}{32}$ solution when diluted to the mark. To this solution, after introducing a drop of phenolphthalein, add a pure solution of the acid in conductivity water until the colour of the indicator is just completely discharged, leaving no free alkali present.

Dilute to the mark with conductivity water and carry out determinations of the conductivity, hence the equivalent conductivity, at dilutions $\frac{N}{32}$ and $\frac{N}{1024}$ exactly as described for acetic acid.

6. **Solubility of almost insoluble salts.**—This may be determined from a knowledge of the value of μ_∞ for the salt at a certain temperature, deduced from the sum of the ionic conductivities of the ions of the salt. (See p. 500.)

Since the salt (*e.g.* $BaSO_4$, AgI, etc.) is almost insoluble, the solution is so dilute that μ_v at dilution v may be taken as equal to μ_∞ itself.

So $$\mu_\infty = \mu_v = \kappa v,$$

v being the number of c.cs. containing 1 gram-molecule of salt.

Hence v is calculated when κ is found.

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Shake the pure substance a number of times with conductivity water, allowing to settle each time and pouring off the clear liquid. Finally shake with a fresh quantity of conductivity water and find the conductivity of the turbid liquid, *deducting that of the water.*

The following table gives the solubility and the molecular conductivity of saturated solutions of a few common "insoluble substances," at 18° C.

Substance.	Solubility in milligrams per litre.	$\mu_{\infty}^{18°}$
AgCl	1·7	120
AgBr	0·4	122
AgI	0·1	121
$SrSO_4$	107	238
$BaSO_4$	2·6	246

7. **Determination of electrochemical equivalents.**—The electrochemical equivalent of an element or radical is the weight of it which is deposited from solution by one coulomb of electricity.

The determination is carried out by electrolysing a suitable salt of the ion and weighing or measuring the quantity liberated by a known current in a known time.

The current is measured either by including an ammeter in the circuit or (best) by means of a silver or a hydrogen voltameter. The latter method of course involves the assumption of the electrochemical equivalent of silver or hydrogen.

The apparatus is that described in Book III., p. 223, Figs. 50 and 51. Suitable solutions for use are:

For Copper.	Copper sulphate crystals -	150 gms.
	Pure sulphuric acid - -	5 c.cs.
	Water to - - - -	1 litre.
For Silver.	Silver nitrate - - -	10 gms.
	Water to - - - -	100 c.cs.

The anode should in each case consist of a plate or stout wire coil of the metal which is being deposited, and it should preferably be enclosed in a muslin bag to prevent small fragments falling into the basin which acts as cathode.

The electrochemical equivalent of an ion is given by

$$\frac{\textit{chemical equivalent}}{96{,}540}$$

for 96,540 coulombs liberate the equivalent weight.

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CHAPTER XI.

ELECTROCHEMISTRY—KINETICS.

1. **Transport numbers of the ions.**—For the full theory and deductions of relations between the relative speeds of the ions and conductivity constants the student is referred to the theoretical text-books.

Briefly, however, when a current is passed through the solution of a salt and electrolysis occurs, though the quantities of liberated elements at the two electrodes are strictly equivalent, yet the concentrations of the salt around those electrodes are found in general to have changed to different extents.

Hittorf explained this by stating that the ions move at different "migration velocities." The student can demonstrate this diagrammatically. We see that

$$\frac{\text{Fall in concentration round anode}}{\text{Fall in concentration round cathode}} = \frac{\text{Rate of cation}}{\text{Rate of anion}}.$$

If u be the velocity of the cation,
and v „ „ „ anion,

then $\frac{u}{u+v}$ is the quantity of electricity carried by the cation compared with $\frac{v}{u+v}$ carried by the anion.

These fractions, sometimes expressed as percentage values, are termed the "transport numbers" of the ions, and may be determined by passing a measured quantity of electricity through a solution of known concentration and finding the change in concentration occurring at one of the electrodes.

Determination of the transport number for silver in a $\frac{N}{20}$ solution of silver nitrate.—This experiment consists of two parts carried out simultaneously.

1. Determination of the total quantity of electricity passing through the cell.

2. Determination of the change of concentration in an electrolyte cell.

(1) **Measurement of quantity of electricity passing.**—This is done by means of a titration voltameter, *i.e.* a voltameter, in which the amount of chemical change to which the electric quantity is proportional, is determined volumetrically, for when the current is very small the deposits produced in silver or copper voltameters are not easily weighed with accuracy.

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A convenient form is as follows, depending on the solution of silver from the positive pole in the electrolysis of a nitrate solution.

The tube *t* shown in Fig. 154 is filled to the level, *a*, with a strong solution of potassium nitrate; the anode *n* consists of a silver wire protected where it passes through the solution by a glass-tube into which it is sealed by Chatterton's compound.

Before being inserted, the surface of the silver electrode must be freshly covered with fine silver electrolytically (see below).

Above the KNO_3 solution at *a*, a layer of $\frac{N}{2}$ nitric acid is poured in carefully, and in it hangs a negative electrode of platinum wire (*m*).

The current to be used may be as much as ·03 ampère per square cm. of anode.

When the current passes, silver goes into solution, one gram-equivalent (108 grams) of silver corresponding to the passage of 96,540 coulombs.

After the current has passed for the requisite time the whole solution is run off into a flask, the apparatus rinsed out with distilled water, and the silver that has dissolved is titrated by means of standard ammonium thiocyanate solution, using ferric alum as an indicator (Volhard's method, *q.v.* in Volumetric Analysis, Book III., p. 243).

(2) **Determination of the change of concentration in the electrolytic cell** (*B*, Fig. 154).—The anode *b* is a silver wire arranged as in the titration voltameter, and silvered before use.

To silver this and the electrode of the titration voltameter simultaneously, prepare a solution of the double cyanide of potassium and silver (by adding KCNaq. to AgCNaq until the precipitate *just* dissolves), and, using a platinum wire as an anode and the silver ends connected with one another as the cathode in the above solution, pass a current of 0·1 ampère for ten minutes. Wash carefully and keep in water till required for use.

The *anode liquid* is a $\frac{N}{20}$ solution of $AgNO_3$ prepared by weighing 2·125 gr. pure silver nitrate solution in 250 grams water.

By using a portion of this solution, the exact strength of a potassium thiocyanate solution (about 4 gm. per litre) should be determined.

The *cathode* (*c*) is a cleaned copper wire, the cathode liquid being a strong solution of copper nitrate, the use of this avoiding any formation of gas on electrolysis.

The cell is shown at *B*, Fig. 154.

When the electrodes have been fixed in position, introduce into the cathode side a saturated solution of copper nitrate acidified with nitric acid, to a depth of about 5 cms.

The silver nitrate solution is made up by *weight* (2·125 gms. of $AgNO_3$ in 250 *gms.* of water). It is added carefully from a pipette to avoid mixing with the copper nitrate, till level with the cross-tube. Then fill the anode side with the silver solution to the level indicated in the figure. Sufficient silver solution should remain to ascertain its titre with $\frac{N}{20}$ thiocyanate.

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Now connect up the apparatus, arranging it so that a current of about ·01 amp. will pass for about two hours. The ammeter A may be switched out by S when the current strength has been adjusted by means of the adjustable resistance R.

Whilst the current is passing:

(i) Titrate a *weighed* portion of the silver nitrate solution with $\frac{N}{20}$ thiocyanate.

(ii) Weigh two beakers for titrating the contents of the transport apparatus.

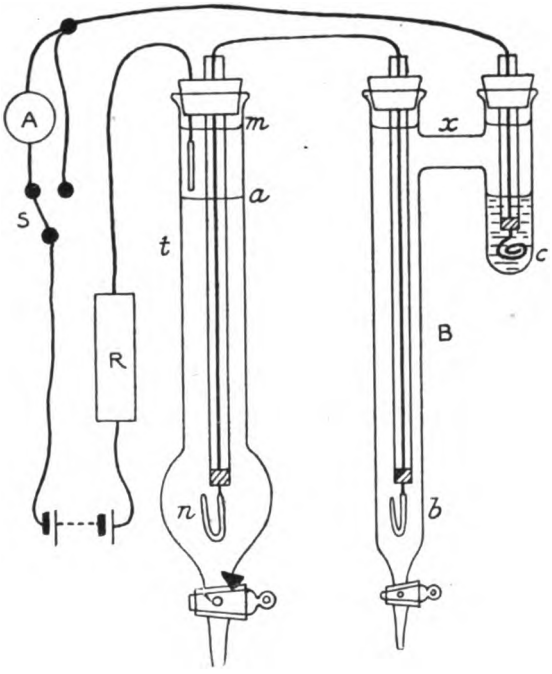

FIG. 154.

After the current has been stopped, pipette out and weigh a small quantity of the solution in the cross-tube at x to ascertain that the concentration there has not altered. (Titrate it.)

Now run about three-quarters of the solution in the anode side b of the transport tube into the weighed beaker, weigh it and determine its silver content by means of the thiocyanate.

Calculate how much silver was originally present in *this weighed quantity* of solution, and hence find the *increase* owing to silver dissolved off the anode—m grams say.

Determine also the silver in the *whole* contents of the titration voltameter—p grams say.

This amount must also have dissolved at the anode in the transport tube.

$\therefore$ $p - m$ grams have migrated away to the cathode side.

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Hence $\frac{p-m}{p}$ represents the migration or transport number of the silver ion. This value should be 0·47.

It follows that $\frac{m}{p}$ is the transport number of the nitranion NO_3. This value should be 0·53.

Other transport numbers may be determined by more or less similar methods, though different metals may be necessary for the cathode. Methods of titration will suggest themselves for the concentrations of such ions as chlorine, bromine, etc. (use of standard silver solutions).

Remember that the solutions and titrations must be by *weight*, for obvious reasons.

2. **Absolute velocity of the ions.** (*a*) *Deduction from conductivity and transport numbers.*—The conductivity is made up of the sum of the ionic conductivities.

If x is the degree of ionisation of a salt, then, there being x equivalents of the anion and of the cation present, and 96540 coulombs being the charge on each gram-equivalent of ions,

$$\lambda = 96540x(u+v),$$

if u and v are the ionic velocities respectively, the ionic conductivities being proportional to these velocities.

Now $$\lambda = \lambda_u + \lambda_v,$$

where λ_u and λ_v are the ionic conductivities, and

$$\lambda_u = 96540xu,$$
$$\lambda_v = 96540xv,$$

so that $$\lambda_u = \lambda T_u \text{ and } \lambda_v = \lambda T_v,$$

where T_u and T_v are the transport numbers.

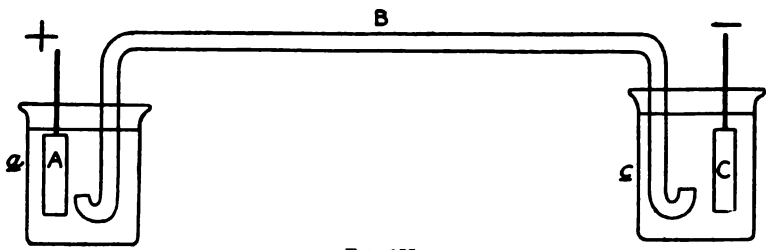

FIG. 155.

From the above expressions the actual velocities can be calculated from the degree of ionisation if the latter is known. Several methods of finding this have already been indicated.

(*b*) *Absolute methods.*—The student is referred to the methods of Lodge (*Brit. Ass. Report*, **1886**, 393, and **1887**, 389); Whetham (*Phil. Trans.*, **1893**, **A.** 337) and others, which will be found in most theoretical text-books, a discussion of which is prevented here by considerations of space.

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The principle of these methods lies in the determination of the rate at which a coloured ion, or the change of colour of an indicator, moves along a tube of solution or of jelly solution.

Lodge's apparatus may be set up as shown in Fig. 155. *A* and *C* are the anode and cathode. *B* is a glass tube about 40 cms. long filled with a 1-2 % solution of agar-agar containing a suitable electrolyte, and if necessary an indicator.

a and *c* are the solutions containing the ion or ions of which the speeds are required.

A voltmeter to measure the applied P.D. should be included.

Suitable solutions to use are :

(i) *For velocities of $H^{\cdot}$ and OH'—*

B contains dilute Na_2SO_4 solution to which a little phenol-phthalein has been added. The left half of this has been coloured pink by a trace of alkali.

a contains dilute H_2SO_4.

c contains dilute NaOH.

(ii) *For velocity of $Cu^{\cdot\cdot}$—*

B, Dilute sulphuric acid or sodium sulphate.

a, Copper sulphate solution (concentrated).

c, Dilute sulphuric acid.

(iii) *For velocity of $Ag^{\cdot}$—*

B, Dilute sodium chloride.

a, Silver nitrate.

c, Dilute hydrochloric acid.

Other solutions to use will readily suggest themselves to the student.

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CHAPTER XII.

CHEMICAL KINETICS.

THE law of Mass Action states that the rate of chemical change is proportional to the molecular concentrations or "active masses" of the reacting bodies.

The simplest case is that of the decomposition of a single body (or the reaction of a body with another which is present in such great relative quantity that its active mass does not sensibly change during the experiment, *e.g.* the case of the saponification of an ester by a large amount of water).

Such a reaction is expressed by a generic equation

$$AB = A + B.$$

Let A be the active mass of AB at the start, and let x be the amount changed at time t. Then as the rate of reaction $\frac{dx}{dt}$ at time t is proportional to $A - x$, we have

$$\frac{dx}{dt} = K(A - x)$$

where K is a constant, or

$$\frac{dx}{A - x} = Kdt.$$

Integrating we have

$$C - \log(A - x) = Kt$$

where C is some constant.

When $t = 0$, $x = 0$. $\therefore C = \log A$.

Hence $$\frac{1}{t} \log \frac{A}{A - x} = K.$$

This equation must hold good for monomolecular reactions.

In the case of bimolecular reactions

$$Ax + By = Bx + Ay$$

the rate depends on *two* reacting bodies.

If A and B be the initial active masses present, and x mols. of each be changed at time t, then

$$\frac{dx}{dt} = K(A - x)(B - x),$$

$$\frac{dx}{(A - x)(B - x)} = K\,dt.$$

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The simplest case is when the substances are initially present in equivalent quantities. The above expression then becomes

$$\frac{dx}{(A-x)^2}=Kdt.$$

On integrating we have

$$\frac{1}{A-x}+C=Kt.$$

If $t=0$ then $x=0$, and $C=-\frac{1}{A}$;

$$\therefore \frac{1}{t}\cdot\frac{x}{A(A-x)}=K.$$

This equation must hold good in the case of a bimolecular reaction.

In many cases a reaction works out, on testing the expressions given by integration, to be of an order different from that expected from the equation, hence valuable information may be gained regarding the steps in a chemical process and the theory of such a process.

One of the best examples to try experimentally is the

1. **Determination of the rate of hydrolysis of an ester by a dilute acid.**—*Hydrolysis of methyl acetate.*—The hydrolysis of an ester by water is very slow but in the presence of dilute acids proceeds rapidly. The extent to which the reaction has occurred can be determined by finding the amount of acid in solution over and above that added to bring about hydrolysis, for we see from the equation

$$CH_3{\cdot}COOCH_3+H_2O=CH_3{\cdot}COOH+CH_3{\cdot}OH,$$

that acetic acid is formed progressively.

This reaction appears *monomolecular* owing to the constant active mass of the water reacting, and its rate depends on the amount of ester present at any moment.

Broadly, then, it is necessary to mix some of the ester with a known volume of acid of known strength, to keep the whole at a constant temperature and to determine at intervals the total acidity of aliquot parts of the solution by titration with baryta water, using phenol-phthalein as an indicator. If the acids are semi-normal and the experiment is carried out at 25° C., the reaction proceeds at a convenient rate and lasts for two or three days in all.

Apparatus and materials required—

1. A thermostat adjusted to 25° C.

2. Vessels for holding the solutions, *e.g.* conical flasks of not more than 100 c.c. capacity, fitted with paraffined corks.

(To paraffin a cork, melt paraffin in a dish, spike the cork on a thin wire and hold it under the paraffin for a few minutes.)

3. The vessels should be steamed before use to minimise the action of water upon them. They can be kept in their places on the shelf of the thermostat by means of pieces of lead-sheet cut and folded as in Fig. 156.

4. Semi-normal solutions of the acid to be used, *e.g.* HCl, H_2SO_4. Their exact strengths should be determined with reference to a solution of baryta preserved in a bottle directly attached to the burette from which it is to be delivered (Book III., p. 235).

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It is best to standardise the baryta against a solution of potassium quadroxalate ($KH_3(COO)_4 . 2H_2O$, 8 grams to the litre), using phenol-phthalein as indicator.

Experiment.—When all the solutions are ready, place the acid solution and a small tube containing methyl acetate, also the conical flasks to be used, in the thermostat to acquire the right temperature.

Place in one of the flasks 80 c.c. of acid solution and a weighed quantity (about 4 c.cs.) of methyl acetate; shake well.

As soon as possible take out 2 c.c. by means of a small pipette, run it into some CO_2-free water to check the reaction, and determine the total acidity, noting the exact time at which the dilution takes place as the starting point of the experiment.

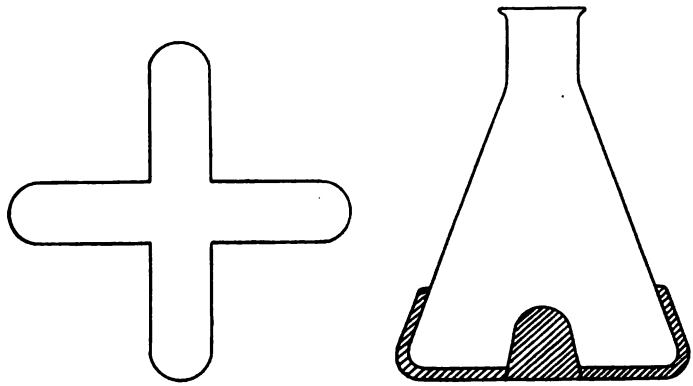

FIG. 156.

At intervals, repeat determinations, the intervals being short at first—say 20 minutes to half an hour, and longer afterwards as the rate slackens. Leave about 10 c.c. in the thermostat for two days or so to get the final state of the system.

Calculation.—Let A be the number of c.cs. of baryta required at the end of the reaction when all the ester is hydrolysed, a_o at the beginning before hydrolysis has occurred, a_t after t minutes.

Then initial concentration of methyl acetate is measured by $A - a_o$.

Concentration at time t is measured by $A - a_t$;

$$\therefore \log \frac{A - a_o}{A - a_t} = Kt,$$

$$K = \{ \log (A - a_o) - \log (A - a_t)\} \cdot \frac{1}{t}.$$

Thus show that the reaction is monomolecular, and find the constant. Then determine K, using other acids of similar concentration and so compare their "*strengths*" or "*avidities*."

2. **Exercises.**—1. Determine the order of reaction of the action of hydrogen iodide and hydrogen peroxide. (Titrate rapidly with thiosulphate and starch.)

2. Determine the influence of ferrous sulphate on the rate of reaction of hydrogen peroxide and hydrogen iodide, and draw a curve showing the values of K resulting from different quantities of ferrous sulphate.

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(Use minute quantities of $FeSO_4$, determine the initial strengths of all substances separately by standard permanganate, and the iodine liberated in the reaction by thiosulphate and starch.

3. **Determination of the rate of occlusion of hydrogen by palladium.**—Clean, dry and heat a small piece of rolled palladium foil in a current of hydrogen, then *in vacuo*.

When pure, seal in a thin tube *in vacuo* and insert in a larger horizontal tube *C* in which a glass striker has been placed. The wide tube is drawn out and sealed to a long narrow tube *D*, 31 inches long, bent at right angles to dip with its free end under a mercury surface. The whole tube *CD* is now filled with pure hydrogen, the end of the long tube sealed, and the whole apparatus set up (Fig. 157).

Break off the tip of the tube under the mercury surface, and carefully break the palladium tube by tilting the apparatus so that the glass striker smashes it.

Note the initial pressure then obtained and the time. Draw a curve showing pressure against time.

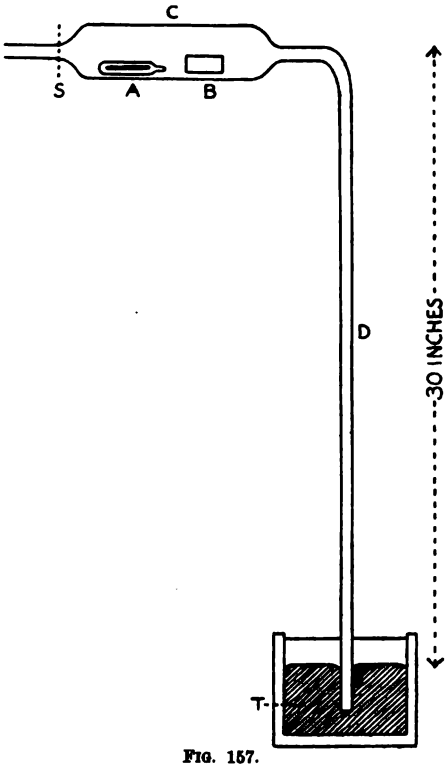

FIG. 157.

4. **Compare the "avidities" of sulphuric and hydrochloric acids** by the rates at which they invert cane sugar. See p. 487.

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CHAPTER XIII.

THE PHASE RULE.

Transition temperatures.—Many crystalline substances are stable in one form below a certain temperature, and in another form above it. The temperature at which this change occurs under ordinary pressure is termed the "transition point." Under these conditions, a discontinuity often occurs in some physical property of the substance; this discontinuity may be utilised for determining the transition point.

Of the various methods available, the principal ones are

(1) Dilatometric methods.
(2) Solubility methods.
(3) Thermometric methods.
(4) Electrical methods.
(5) Optical or other methods.

However *any* physical change which occurs at the transition point will afford a method.

(1) **Dilatometric method.**—This method utilises the change in volume of a substance due to change in temperature, and determines the transition point by obtaining the temperature at which a discontinuity or change occurs in the rate of volume-change.

Apparatus.—The dilatometer consists essentially of a bulb *A* of about 50 c.c. capacity to which is fixed a long capillary tube *B* provided with or placed in front of a millimetre scale.

Method.—Through *C*, the open end of *A*, introduce dry crystals of the substance (*e.g.* Glauber's salt) until *A* is nearly full. Push away the crystals from the immediate neighbourhood of *C* and seal off the latter.

To make a determination it is necessary to introduce a liquid such as petroleum oil in order to fill the spaces between the crystals and extend into the capillary; this liquid must not have any action on the salt employed.

To fill with petroleum, another tube *D*, as shown in Fig. 158, is attached to the open end of *B*, the latter being placed vertically. Corked on to the top of *D* is a T-piece tube, *E*, connected at *F* with a filter-pump, and through the side arm *G* to the air, the latter being clipped when necessary with the aid of a piece of pressure tubing and a clip.

Introduce a few c.c. of petroleum into *D*, cork, close the clip, and exert suction by means of the pump. Then open the clip to introduce air; the latter forces the petroleum down *B* into *A* to take the place of the air sucked out.

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Repeat, and finally arrange that the level of the petroleum stands in the capillary near to *A*, after eliminating any air-locks, etc.

Now place the bulb *A* in a bath of water and heat very slowly, noting the readings of the meniscus at every degree rise in temperature.

Draw a graph and note the point *A* (Fig. 159) at which the rate of change of volume alters temporarily. After it has settled down again to a steady rate, allow to cool and note the reverse readings, making a determination of the temperature corresponding to point *B* where the rate of volume change alters again.

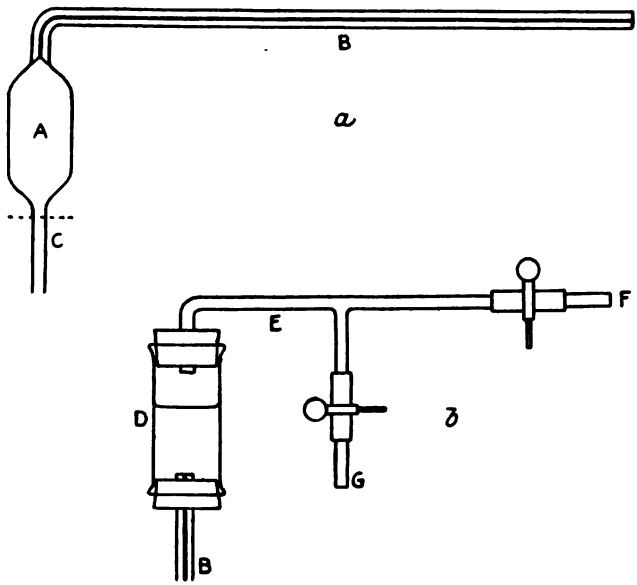

FIG. 158.

The mean of *A* and *B* will give the transition point, a slight "lag" having taken place in both cases. The result for Glauber's salt is about 33° C., at which temperature the decahydrate and anhydrous salt are in equilibrium.

(2) **Solubility method.**—All that is necessary in this case is to make solubility determinations at different temperatures for the two modifications.

Method.—Supposing sodium sulphate be used, determine the solubility by the direct method as already described in a previous chapter at 20° C., 25° C., 30°, 35°, 40°, 45°, and draw the curve.

It will be noticed that the curve for the first three readings does not coincide with that for the others, but that the two curves, if interpolated, will cross. This indicates that at the transition point, the solubilities of the decahydrate and anhydrous salt are similar, but that at all other temperatures, if they could both exist, the solubility of the unstable phase would always be higher than that of the stable phase.

After making a rough determination, a more careful set of readings should be taken in the neighbourhood of the point, it being ensured that at temperatures near the transition point no unstable phase exists. The solution

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in contact with the *stable* phase only should therefore not be heated or cooled (as the case may be) beyond the transition temperature.

(3) **Thermometric methods.**—Just as latent heats of fusion cause a cessation in rise of temperature of a steadily heated substance during the change from one state to another, and in the fall of temperature of a steadily cooling body under similar conditions, so also the same effect is produced in many instances on cooling, or heating regularly, a substance undergoing transition.

Place a boiling tube, containing the powdered substance into which a thermometer is inserted, in a bath, and warm slowly, say at the rate of about one degree per five minutes, after maintaining at a constant temperature of 25° C. for half an hour until everything has attained this temperature.

Note the rate of rise of temperature of the salt and record by a graph. Afterwards allow to cool, by these means obtaining a result similar to that obtained in the dilatometric method.

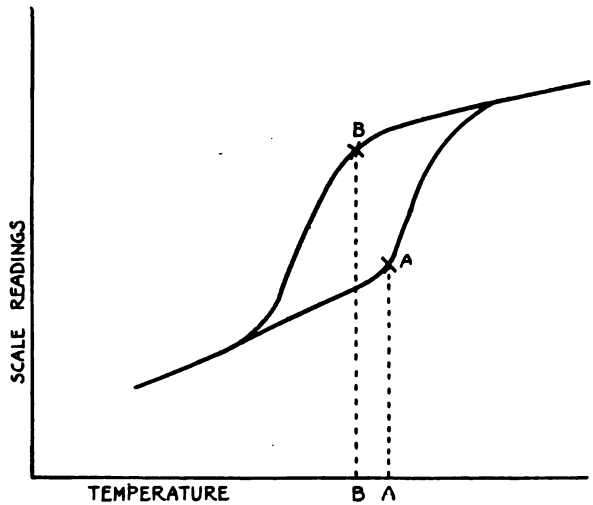

FIG. 159.

(4) **Electrical methods.**—The conductivity of a solution of a salt at various temperatures may be measured and results deduced from a graph. Through the transition point one can obtain a graph, similar to that obtained in Method (2), solubility.

One of the most instructive methods is, however, by means of a *concentration cell* formed from a metal and saturated solutions of two forms of the same salt, *e.g.*, zinc sulphate in its hexa and hepta hydrated forms, with two zinc electrodes.

In all cases, if a metal dips into a solution of one of its salts, a definite potential difference exists between the metal and the solution, the magnitude of which depends on the ionic concentration of metal in the solution. So that a "concentration cell" of the type

Metal	dilute solution of salt	concentrated solution of salt	metal

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will have a definite E.M.F. owing to the fact that the *ionic* concentration in the *dilute* solution is greater than that in the concentrated solution.

In the case of $ZnSO_4$, $6H_2O$ and $ZnSO_4$, $7H_2O$, the stable form below the transition point (the hepta-hydrate) has a definite solubility whilst the stable form above the transition point (the hexa-hydrate) has another, the two solubilities coinciding at the transition point itself.

Hence the system:

Zn	Saturated solution, $ZnSO_4$, $7H_2O$	Saturated solution, $ZnSO_4$, $6H_2O$	Zn

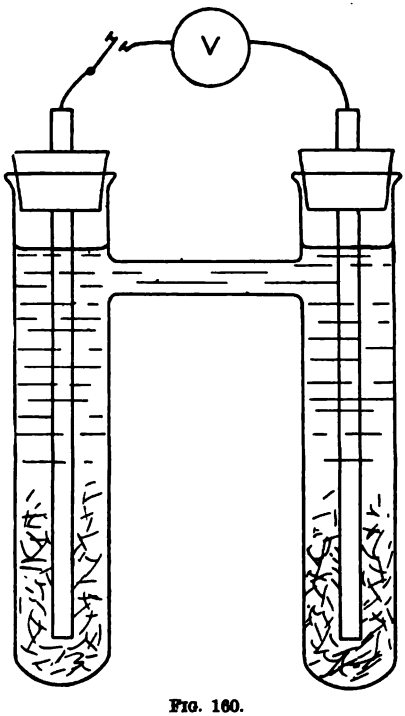

FIG. 160.

will have a definite E.M.F. except at the transition point for such temperatures as those at which the salt is capable of existence in its two forms simultaneously owing to one form being meta-stable.

At the transition point the E.M.F. passes through zero from positive to negative.

Determination of the transition point.—By preliminary trials on the lines given below it may be easily established that the transition point is in the neighbourhood of 40° C.

Take an H-tube closed at the lower ends, or preferably, two tubes with side arms, the tubes being about 10 cm. long and 1·5 to 2·0 cm. wide.

In the bottom of each, place finely-powdered $ZnSO_4 . 7H_2O$ till the tube is nearly half full, and fill to the side arm with a saturated solution of the salt. Stir till the whole ingredients are in the form of a thin paste, and insert two

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rods of pure zinc as electrodes sealing them in at the top and immersing them well into the paste in each arm. Now heat one side of the H-tube or one of the two tubes as the case may be, in a bath to about 55° C., and maintain this temperature for half an hour or more, afterwards allowing to cool slowly to about 28° C. During this process see that the other side is kept cool, screening it if necessary.

When cool, connect the side arms if two tubes are being used, and in any case see that the solutions in the two branches are in contact across the connection.

The state of affairs then will be that the arm which has been heated will contain $ZnSO_4$, $6H_2O$ (unstable and more soluble), whilst the other has $ZnSO_4$, $7H_2O$ (stable and less soluble).

Connect the two zinc electrodes through a switch to a high resistance sensitive galvanometer or milli-voltmeter, and immerse the whole H-tube in a bath of water at 30° C. for 30 minutes. From time to time after this close

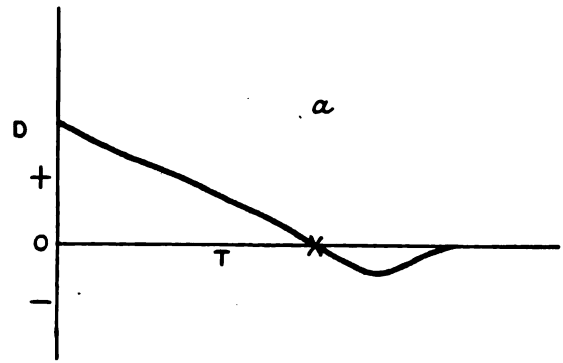

FIG. 161 (*a*).

the switch and note the deflection of the voltmeter, noting the readings at 30°, 35°, and then every degree or more frequently as the deflection decreases.

The heating of the bath must be carried out extremely slowly, say one degree per ten minutes.

Presently there will be a temperature at which the deflection is zero; at higher temperatures the deflection will be reversed, but will again gradually decrease with rising temperature owing to the steady change of the hepta-hydrate to the hexa-hydrate in the previously untreated side of the tube.

Draw a graph, marking deflections as ordinates, and temperatures as abscissae. The transition point is given by the point on the curve at which the axis of time is cut (Fig. 161 (*a*)).

It may occur that owing to some impurity or the use of some wax, etc., the voltmeter will never show a zero, but some constant E.M.F. will be present.

In this case, instead of the axis of time through the origin being cut by the deflection curve, there will be another axis to which the curve will eventually form a tangent, as in Fig. 161 (*b*). The point at which this axis is

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cut will then equally well give the transition temperature, the deflection falling to a minimum and again increasing to a constant value.

(5) **Optical and other methods.**—Examination of a crystalline substance under the microscope on a plate whose temperature is regulated will give interesting results. Try this with ammonium nitrate.

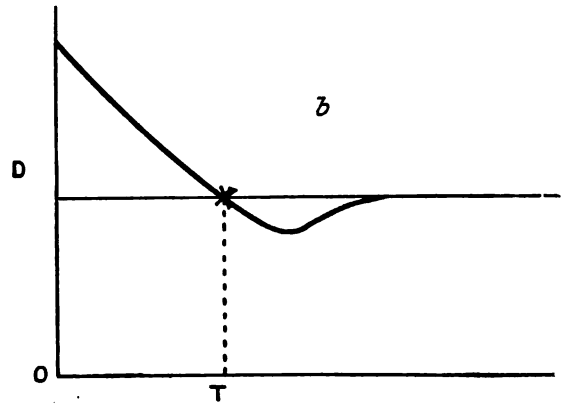

FIG. 161 (*b*).

Other substances give obvious colour changes, *e.g.* mercuric iodide and cuprous mercury-iodide (*q.v.* pp. 38 and 87).

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Logarithms.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
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11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

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											1	2	3	4	5	6	7	8	9
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56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
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77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
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82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
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84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
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98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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ATOMIC WEIGHTS OF THE ELEMENTS.

International Atomic Weights for 1920.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27·1	Mercury	Hg	200·6
Antimony	Sb	120·2	Molybdenum	Mo	96·0
Argon	Ar	39·9	Neodymium	Nd	144·3
Arsenic	As	74·96	Neon	Ne	20·2
Barium	Ba	137·37	Nickel	Ni	58·68
Beryllium or Glucinum	Be	9·1	Niton (Ra-emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·008
Boron	B	10·9	Osmium	Os	190·9
Bromine	Br	79·92	**Oxygen**	**O**	**16·00**
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·1	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenion	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	70·1	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum, *see* Beryllium			Tantalum	Ta	181·5
			Tellurion	Te	127·5
Gold	Au	197·2	Terbium	Tr	159·2
Helium	He	4·00	Thallium	Tl	204·0
Holmium	Ho	163·5	Thorium	Th	232·15
Hydrogen	H	1·008	Thulium	Tu	168·5
Indium	In	114·8	Tin	Sn	118·7
Iodine	I	126·92	Titanium	Ti	48·1
Iridium	Ir	193·1	Tungsten	W	184·0
Iron	Fe	55·84	Uranium	U	238·2
Krypton	Kr	82·92	Vanadium	V	51·0
Lanthanum	La	139·0	Xenon	X	130·2
Lead	Pb	207·20	Ytterbium	Yb	173·5
Lithium	Li	6·94	Yttrium	Y	89·33
Lutecium	Lu	175·0	Zinc	Zn	65·37
Magnesium	Mg	24·32	Zirconium	Zr	90·6
Manganese	Mn	54·93			

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